M 2015

U.PORTO
FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

OPTIMIZATION OF THE ANALYSIS OF GASOLINES WITH GC×GC

ANDRÉ MORGADO LOPES

DISSERTAÇÃO DE MESTRADO APRESENTADA
À FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO EM
ENGENHARIA QUÍMICA

Mestrado Integrado em Engenharia Química

Optimization of the analysis of gasolines with GC×GC

Master's Degree Thesis

of

André Morgado Lopes

Developed within the purview of the Dissertação course

carried out at

IFP Energies nouvelles

Supervisor at FEUP: **Prof. Arminda Alves**

Supervisor at IFPEN: **Dr. Vincent Souchon**

Departamento de Engenharia Química

July 2015

Acknowledgements

First of all, I would like to express my profuse appreciation for my project coordinator and GC laboratory manager, Dr. Vincent Souchon to whom I owe an overwhelming amount of gratitude for, not only providing me the opportunity to take up this challenge but also for his expert guidance, constant support and crucial advice and criticism throughout the entire project.

I would also like to thank Prof. Arminda Alves for her assistance in the writing, structure and proof-reading of this manuscript.

I am hugely indebted to every single person working in the Gas Chromatography laboratory at IFPEN for coming to my aid in countless situations, for helping me cross the language barrier and making me feel welcome in an excellent working environment. It was truly a pleasure to work among such people.

Finally, I would like to acknowledge Bruno Sousa and Joana Rocha for their inexorable support and for the numerous insightful discussions during the course of each stage of the project.

Abstract

Two-dimensional comprehensive gas chromatography (GC×GC) has proven to be a very promising technique for the analysis of complex samples such as diesel oils but is not yet used for the study of gasolines. Using both cryogenic and microfluidic modulation, many combinations of columns were tested in order to optimize the operation parameters for the analysis of gasolines for each modulation system and for normal and reverse configurations. Mid-polarity stationary phases with low minimum working temperature limits proved to be the best at achieving an efficient separation of the gasoline samples in question, both as the second dimension in normal configuration and as the first in reverse configuration. Cryogenic modulation showed a clear advantage in resolution and versatility while microfluidic modulation excels at ease of use, convenience and economic viability. The optimized configurations were used for a variety of gasoline samples and their detailed hydrocarbon analysis using data obtained with a mass spectrometry detector hyphenated to GC×GC.

Keywords: GC×GC; two-dimensional comprehensive gas chromatography; cryogenic modulator; microfluidic modulator; normal configuration; reverse configuration; gasoline analysis

Resumo

A cromatografia gasosa bidimensional abrangente (GC×GC) tem provado ser uma tecnologia promissora no que toca a análise de amostras complexas como gasóleo mas não é ainda utilizada para estudar gasolinas. Usando tanto a modulação criogénica como microfluídica, várias combinações de colunas foram testadas de forma a otimizar os parâmetros de operação para a análise de gasolinas em cada sistema de modulação e nas configurações normal e inversa. Fases estacionárias de polaridade média com baixos limites mínimos de temperatura de operação foram as melhores a conseguir uma separação eficaz das amostras de gasolina em questão, tanto na segunda dimensão em configuração normal como na primeira em configuração inversa. A modulação criogénica demonstrou uma clara vantagem em termos de resolução e versatilidade, enquanto a modulação microfluídica distingue-se pela sua facilidade de utilização, conveniência e viabilidade económica. As configurações otimizadas foram utilizadas numa variedade de amostras de gasolina incluindo a sua análise detalhada de hidrocarbonetos usando dados obtidos através da deteção por espetrometria de massa.

Palavras-chave: GC×GC; cromatografia gasosa bidimensional abrangente; modulação criogénica; modulação microfluídica; configuração normal; configuração inversa; análise de gasolina

Declaration

Declaro, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.

(I hereby declare, under oath, that this work is original and that all non-original contributions were properly referenced with identification of the respective sources.)

(Lyon, 06/07/2015)

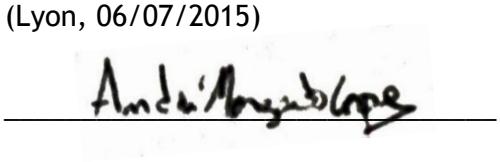


Table of Contents

List of Images

List of Tables

Notation and Glossary

Equation variables

T	Tailing Factor	
P_{mod}	Modulation pressure	psi
Q_{1D}	First dimension flow rate	ml/min
Q_{2D}	Second dimension flow rate	ml/min
t_m	Modulation time/period	s
t_i	Injection time	s
ID	Internal diameter	mm
l	Length	m
a	Width of the left side of a peak at 10% height	s
b	Width of the right side of a peak at 10% height	s
m/z	Mass number over charge number	

List of abbreviations

GC	Gas Chromatography
GC×GC	Comprehensive Two-Dimensional Gas Chromatography
HDT	Hydrotreatment
FID	Flame Ionization Detector
LPG	Liquefied Petroleum Gas
MS	Mass Spectrometry
TOFMS	Time of Flight Mass Spectrometry
FCC	Fluid Catalytic Cracking
DHA	Detailed Hydrocarbon Analysis
PONA	Paraffins, Olefins, Naphtenes, Aromatics
DCPD	Dicyclopentadiene
CFT	Capillary Flow Technology
FFF	Forward Fill/Flush
RFF	Reverse Fill/Flush

1 Introduction

1.1 Description of the Institution

IFP Energies nouvelles (IFPEN) is a public research and training institution. It has an international scope, covering the fields of energy, transport and the environment. From research to industry, technological innovation is central to all its activities.

As part of the public-interest mission with which it has been tasked by the public authorities, IFPEN focuses on providing solutions to take up the challenges facing society in terms of energy and the climate by promoting the emergence of a sustainable energy mix as well as creating wealth and jobs by supporting French and European economic activity, and the competitiveness of related industrial sectors.

An integral part of IFPEN, its graduate engineering school prepares future generations to take up these challenges.

The project was developed at the Gas Chromatography laboratory at IFPEN.

1.2 Framing of the Project

The petroleum industry is one of the most powerful forces in global economics and it promises to maintain its supremacy for years to come (Finley 2012). Therefore, a lot of analytical chemistry in the past decades has been focused on the analysis of petroleum and its derived products in order to achieve a more accurate characterization and to improve refinery processes in order to meet the global demand as well as more and more drastic environmental regulations.

The massive variety and complex composition of these hydrocarbon matrices makes it a veritable challenge to separate and completely quantify its numerous individual compounds. While capillary gas chromatography (GC) proved to be a reference technique in both quantitative and qualitative analyses of volatile samples such as petroleum-based products, it still wasn't powerful enough to resolve every single component in a given hydrocarbon mixture: compounds with similar volatilities, especially many isomers, still reached the end of the chromatographic column at around the same time (a phenomenon known as "co-elution") even with optimum separation conditions (Guiochon et al. 1983).

The failure to separate all the compounds in a given mixture led researchers to pursue different and innovative ways to set up a GC experiment. Elder, Jr. et al. (1986) proposed that a better separation could be achieved by using two columns instead of one single-column in conventional GC setups. Using a valve system to retrieve a small fraction of the sample at the end of the

first chromatographic column and redirecting it to second column - a technique known as "heart-cutting" - furthered the quest for the maximum achievable resolution in the analysis of hydrocarbon mixtures. Heart-cutting's main benefit is that it allows the use of two columns that interact with the compounds in the mixture by the way of different chemical properties (such as polarity or volatility), which meant that compounds that would usually co-elute could now be separated. The drawback to this technique is that it did not allow a full characterization of the whole injected sample, only the cut portion.

Comprehensive multidimensional gas chromatography was developed to address this particular limitation (Phillips, Xu 1995). In comprehensive two-dimensional gas chromatography (GC×GC) systems, two columns (commonly referred to as "dimensions") with different retention mechanisms are connected in series by a modulator, whose function is to quickly collect very small samples at the end of the first column and re-inject them into the second column, much like the heart-cutting technique. The main difference is that, as opposed to heart-cutting which could only take one or several small parts of the entire sample to the second column, the modulator provides a way for the entirety of the mixture to be subjected to two separations (Schoenmakers et al. 2003).

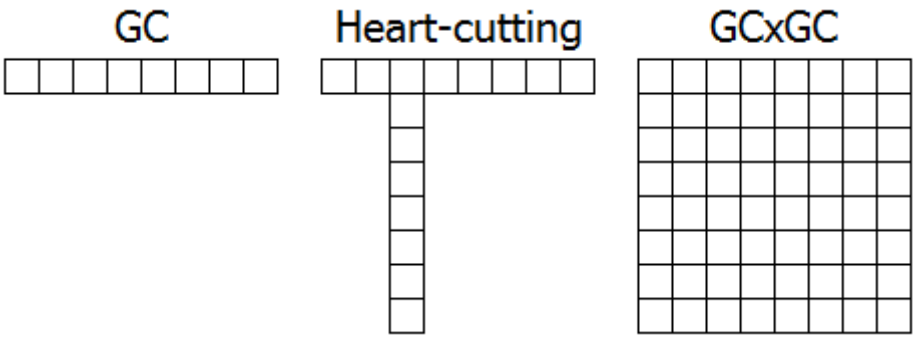


Figure 1.1 *– Theoretical illustration of the separation space for different techniques (adapted from Bertoncini et al. 2013)*

This leads to a huge increase in the separation space which allows for a better separation between the many different compounds present in a complex hydrocarbon mixture, thus facilitating the thorough characterization of petroleum derived products. Coupling such a system to a mass spectrometer or element specific detectors such as a sulfur chemiluminescence detector also allows for the identification of the separated compounds or compound families.

GC×GC is, in fact, already used to some extent in the petroleum industry to analyze heavy cuts of the petroleum distillation process such as diesel fuels (Adam et al. 2010) and vacuum gas oil (Dutriez et al. 2010). Various review articles (Nizio et al. 2012; Vendeuvre et al. 2007) have also been released detailing several possible setups and applications for the analytical

technique, however, it has seldom been considered as a tool for gasoline analysis, which is, to this day, done with traditional one-dimensional GC which has always been considered efficient for this type of product.

1.3 Project Objective

This focus of this project is assessing the viability of several GC×GC setups and optimizing the method parameters for the analysis of gasoline samples. These samples include Reformate, post-Fluid Catalytic Cracking (FCC) gasolines, Hydrotreated gasoline, Pyrolysis Gasoline and Oligomerization Gasoline. The aim of the study is to obtain the best conditions for the separation of the compounds present in such samples.

The most important point of study is the effect of modulation. Two GC×GC machines with different modulation processes are used: cryogenic and microfluidic. The assessment of their strengths and weaknesses is imperative toward the achievement of the best separation conditions, as is the configuration of stationary phases and several other parameters.

1.4 Contributions of the Project

The project was developed in order to find the best possible conditions for the analysis of gasolines with GC×GC and, as such, has great potential in facilitating the creation of standardized methods for the routine and in-line analysis of different gasoline types.

Easier qualitative and quantitative analysis will, in turn, allow a better understanding of chemical reactions involved in refining processes, help in catalyst development or chemical engineering studies in order to provide eco-efficients processes. The results obtained from this work have direct consequences for other R&D divisions of IFPEN that are working to develop new catalysts for gasoline refining.

1.5 Document Structure

In chapter 2, there is a short introduction to the petroleum refinery processes and several different types of gasoline produced in those processes as well as a theoretical description of the multidimensional comprehensive gas chromatography technique, particularly the different modulation types and their basic functioning methods.

Chapter 3 focuses on the description and characterization of the setups used in the experimental part of the project.

Chapter 4 contains the outcomes of the tests performed in each of the different setups. The results of the analysis parameters optimization in several different configurations are presented, explored and discussed in detail.

Some examples of real analysis applications using some of the best optimized configurations attained during the project are studied in chapter 5.

Chapter 6 concludes the report with some final thoughts on the accomplishments of the development, the worth of the information attained from the project results and some perspectives towards possible future work.

2 Context and State of the Art

2.1 Crude oil refining and gasoline properties

Refineries have only one purpose which is the production of valuable products, for the most part fuels, in agreement with the market demand. These fuels can be liquefied petroleum gases (LPG), gasolines, diesels fuels or domestic fuels. However, refineries can have different configurations depending on the crude oil to be refined. This happens because not all petroleum is created equal: hydrocarbon fractions by weight and quantities of heteroatoms such as sulfur and nitrogen vary according to their geographical and geological origin. Some refineries are also more oriented toward the production of diesel whereas others focus on the production of gasoline, thus having different structures and processes.

In the process of refining crude oil, the atmospheric distillation process first separates compounds into several fractions by molecular weight. A refinery has an extremely complex system but Figure 2.1 offers a simplified explanation of some of the most common refining steps in the production of commercial gasoline.

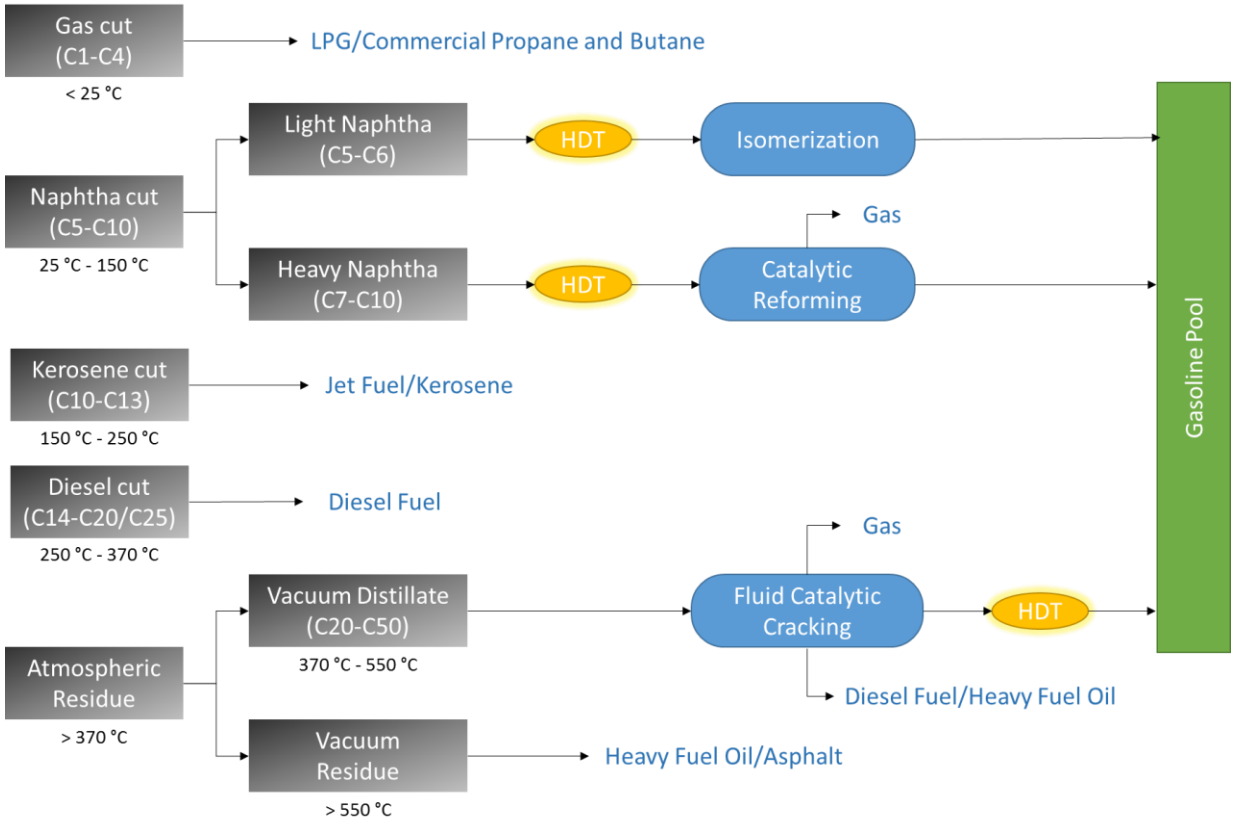


Figure 2.1 *– Simplified schematic of the refining of crude oil into gasoline*

What eventually ends up in the gasoline pool is a mixture of hydrocarbons with number of carbon atoms between 4 and 10.

2.1.1 Properties and composition of gasolines derived from different processes

Different types of gasolines exist in a refinery, depending on the process from which they are produced. Each of them has different characteristics and, as such, are comprised of different hydrocarbons in varying concentrations. The gasoline types described below are the ones that have been analyzed during this work.

2.1.1.1 FCC effluent

Fluid Catalytic Cracking is a gasoline refining process by which hydrocarbons with a large molecular mass, typically found in vacuum gas oil, are "cracked" into smaller molecules so as to produce a more valuable gasoline mixture with a high octane rating. This is achieved with the use of a zeolite-based catalyst in the form of powder, which allows it to have a fluid-like behavior. This allows it to be easily removed from the reactor so that the coke that is deposited in the catalyst can be burned off, after which the regenerated catalyst returns to the reactor. This assures the continuous operation of the FCC reactor (Toulhoat, Raybaud 2013, p. 543). The FCC effluents usually have high octane numbers due to being mostly composed of aromatics and iso-paraffins.[1]

2.1.1.2 Hydrotreated gasoline

Hydrotreatment or hydrodesulfurization is a refining step that immediately follows a variety of other processes, including FCC. Its objective is to reduce sulfur content in the gasoline to within the imposed regulations. The gasoline hydrotreating process occurs under hydrogen pressure and high temperature and in the presence of a catalyst. Although it is possible to hydrotreat a feedstock with high sulfur content before the fluid catalytic cracking phase, it is very common for it to be done after FCC for example thanks to the Prime-G process (Speight 2006, pp. 450–452).

2.1.1.3 Reformate

The reforming process comprises an intricate series of reactions that have a final objective of increasing the content of aromatic compounds in the gasoline mixture. The reforming reaction happens in the presence of hydrogen, which provides the appropriate conditions for the desired reactions while protecting the catalyst from the deposition of carbon. Despite this excess of

[1] In the context of the petroleum industry, hydrocarbon nomenclature is different from the IUPAC conventions. Alkanes are usually referred to as "paraffins", compounds with a double bond are called "olefins" (two double bonds – "diolefins"; cyclic – "cyclo-olefins"), saturated cyclic hydrocarbons are "naphthenes" and compounds with a benzene ring such as alkylbenzenes are called "aromatics" (for two benzene rings – "diaromatics" and so on).

hydrogen, dehydrogenation is still the most prevalent reaction in the reforming process, which means that even more hydrogen is produced (Speight 2006, pp. 454–455).

2.1.1.4 Pyrolysis gasoline

Ethylene and Propylene are often produced by naphtha cracking in petrochemical complexes. In this process, pyrolysis gasoline, also known as Pygas, is also created. It has a high concentration of benzene and is mostly used as a gasoline blending mixture due to its high octane number (Javed 2012).

2.1.1.5 Oligomerization gasoline

As the name suggests, Oligomerization Gasoline is produced by the process of oligomerization (limited polymerization) of light olefins (C3 to C5, usually propylene or butylene), which are produced by catalytic cracking or steam cracking.

2.1.2 Current gasoline detailed analysis methods

As has been pointed out, the complex nature of gasoline and the sheer massive number of possible hydrocarbon isomers make it virtually impossible to completely separate and identify ever single compound present in such mixtures. Current methods of Detailed Hydrocarbon Analysis (or "DHA") correctly classify compounds in their respective families. This kind of analysis is usually performed following the ASTM International standards D6729 or D6730 which make use of high resolution 1D gas chromatography. In this method, a column of 100 m in length with a dimethylpolysiloxane (non-polar) stationary phase is used. A similar, if slightly less powerful, method (ASTM D6733) which relies on a 50 m column (PONA column) and has been developed in the past years at IFPEN. Results obtained from such methods are close to single component identification even if some unavoidable co-elutions still exist.

At this time, only one article has been published discussing the analysis of gasolines with GC×GC (Seeley et al. 2007). However, since the technique has proven successful at the detailed study of heavier samples such as diesel or vacuum gas oil, there is great interest in developing methods for gasoline analysis.

2.2 Basics on comprehensive bidimensional chromatography (GC×GC)

2.2.1 Classical GC concepts

Here is a short description of the basic concepts of gas chromatography that need to be explained before going to multidimensional chromatography. Different compounds elute through capillary columns and take more or less time depending on their affinity to the stationary phase which is a thin layer of liquid polymer that is bound or coated on the inner wall of the capillary column. This affinity is a function of the interactions that the compounds

in the mobile phase have with the functional groups that are present in the film of the stationary phase and are usually related to chemical bonding (Van der Walls forces, hydrogen bonds and ionic bonds). This affinity also depends on the temperature at which the columns are during the analysis, in fact, oven temperature has a great effect on the retention time of different compounds. The order in which compounds elute through the column may even change depending on the temperature programming of the analysis. When compounds reach the end of the second column, they arrive at a detector which responds to their presence and provides a signal proportional to their quantity. For a generic compound, ideally, a peak that is in the shape Gaussian curve is observed, though in reality there may be some deviations.

Concepts such as resolution, efficiency and resolution remain from traditional gas chromatography, though adapted to fit the bidimensional space. Understanding these concepts in one-dimensional GC is very important toward grasping the GC×GC revision of the concepts. Efficiency remains the ability of a certain setup to create sharp, narrow and intense peaks rather than large ones, which may potentially cause co-elutions. Column length has a great effect on the efficiency of the separation and the same is true for GC×GC but increasing column length is not always the best option as it also increases elution time and therefore analysis time. This has a greater impact on bidimensional systems since the second dimension separation depends on what happens in the first.

Selectivity is the ability of a column to separate two compounds thanks to different interaction strengths with the stationary phase. An increase in selectivity means that there is more time between the elution of two compounds. The efficiency and selectivity concepts in one-dimensional GC are better understood when visualized, so Figure 2.2 illustrates them and their relation to resolution.

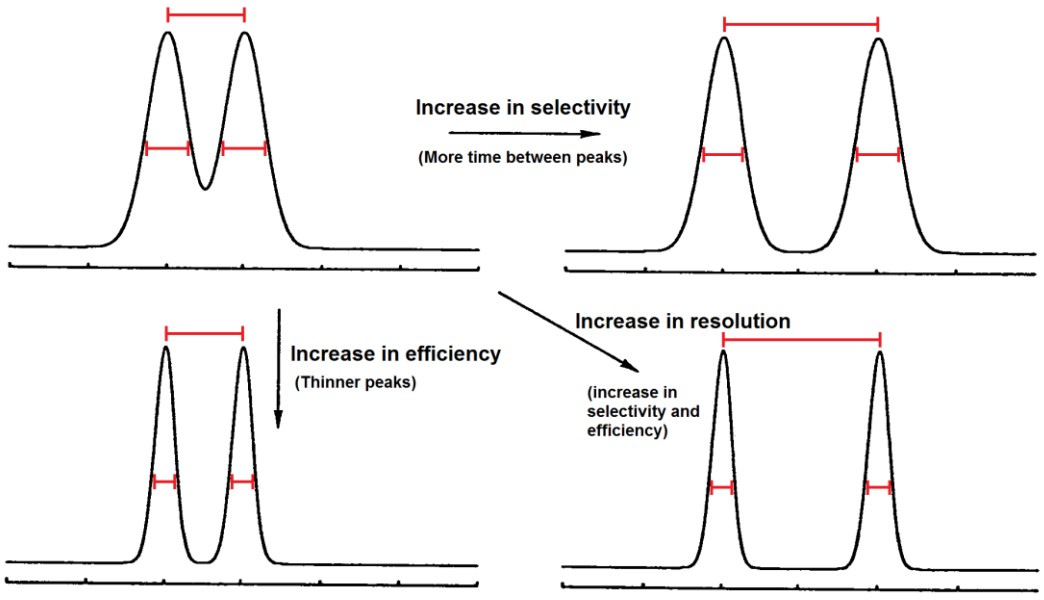


Figure 2.2 *– Selectivity and efficiency in traditional GC and their effect on resolution*

Resolution in GC is a pretty straightforward criterion to evaluate the quality of the separation of two compounds. It takes into account difference in retention times and the peak widths of two compounds, effectively combining the concepts of selectivity and efficiency into one parameter. When translated to GC×GC, the calculation of resolution gets slightly more complex. Adding a second dimension means that one compound is not directly in front or behind the others, meaning that the calculation becomes a tridimensional issue considering the retention times and peak widths in both columns plus the intensity of the peaks. Another issue is that there might more than one neighboring peak between the two which are being analyzed, which affects the shape that the signal takes in two dimensions.

2.2.2 Modulation

2.2.2.1 Role of the modulation system

The crux of the GC×GC, the process of modulation aims at dividing the sample as it reaches the end of the first dimension and then inserting these smaller fractions into the second column. As noted before, this allows the entire sample to be subjected to two separations.

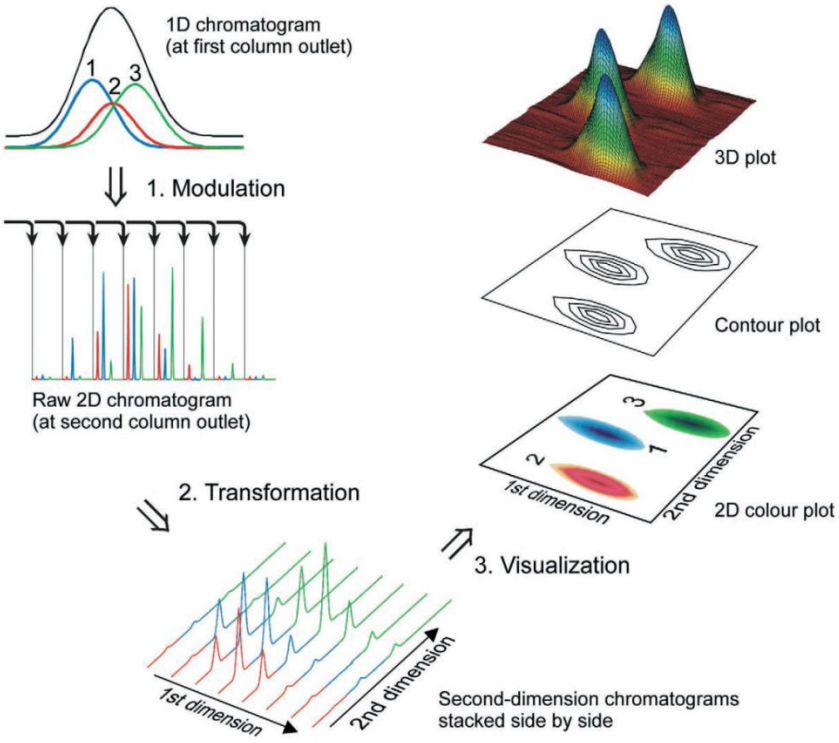


Figure 2.3 *– 2D chromatogram conversion, processing and visualization (Dallüge et al. 2003)*

In Figure 2.3, the only peak shown in the 1D chromatogram is the larger, black-colored peak, composed of three co-eluted compounds. In step 1., this peak is modulated – small fractions of the sample that arrive at the first dimension outlet are introduced into the second column. The three co-eluted compounds now have different retention behaviors in the second dimension, which means that they will elute at different times. This, effectively, eliminates the co-elution

and allows the three compounds to be separated, unlike what would happen with a classical chromatography setup. In the end of the analysis, the raw data reaches the software as a chromatogram that is divided into smaller chromatograms with the length of the modulation period. These chromatograms are arranged side by side (2.) and the software converts this into a 2D image (3.).

There are several types of modulation techniques however the two main types are cryogenic and valve-based modulation. Both techniques have their advantages and disadvantages, however both are currently used for different purposes.

2.2.2.2 Cryogenic modulation

The operation principle behind cryogenic modulation is a simple but effective one: a jet of cryogenic fluid periodically hits the inlet of the second chromatographic column, trapping the compounds that are eluting at that moment, focusing them into a small concentrated quantity of compounds. These compounds then move on through the second column. A representative example is the CO_2 dual-jet modulator developed by Beens et al. (2001) and shown in Figure 2.4.

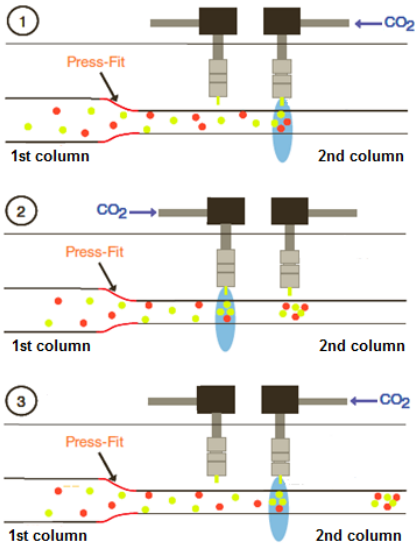


Figure 2.4 *– CO_2 modulator functioning cycle (adapted from Bertoncini et al. 2013)*

At first (1), the second CO_2 jet traps and focuses compounds eluting from the first dimension. Then (2) the first jet fires, inhibiting the following compounds from re-mixing with the first modulated compounds. At the same time, the second jet stops firing, which releases the trapped compounds, thus allowing them to be injected in the second column. The cycle then restarts (3) and repeats throughout the analysis.

Another type of modulator, manufactured by Zoex, uses liquid nitrogen instead of carbon dioxide as the cryogenic fluid and also introduces a hot jet into the modulation system, thus allowing for a more efficient re-injection of compounds into the second dimension. The column

is arranged in a loop around the modulator, as shown in Figure 2.5, which effectively makes the system work as if two jets are present, since the compounds go through and get hit by the jets twice within each modulation period.

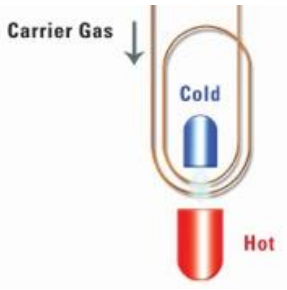


Figure 2.5 *– Zoex modulator column setup*

One advantage of this type of modulator is that they have no moving parts, which makes them robust and reliable, however the use of cryogenic fluid means that they are also a more expensive option. The modulator used in the tests for this project is characterized and explained in section **Erro! A origem da referência não foi encontrada.**, along with a technical description of the remainder of the cryogenic modulation setup.

The main disadvantage associated with the use of these types of modulators is the cost of the cryogenic fluid (in this case liquid nitrogen), which makes this option financially less viable than other modulation techniques. Additionally, the appropriate infrastructure – including liquid nitrogen tanks, piping and level controllers - is required, further increasing the cost.

2.2.2.3 Valve-based modulation

The use of valve based systems for modulation stems back to the initial practice of heart-cutting, which involved a simple valve switch called a Deans switch, illustrated in Figure 2.6.

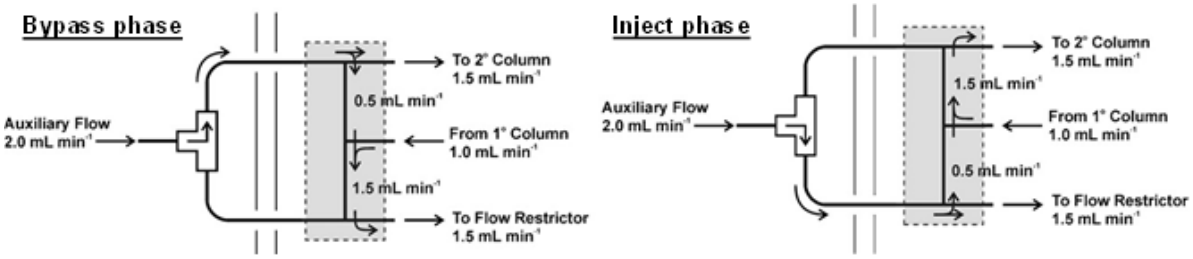


Figure 2.6 *– Schematic and working principle of a Deans switch (Seeley et al. 2007)*

Compounds would elute into a flow restrictor until the proper fraction of compounds to be analyzed in the second dimension arrived at the end of the first column. The auxiliary flow would then be diverted, taking the compounds from the first column into the second column rather than the flow restrictor. This is not considered a proper modulator since it does not allow for a comprehensive analysis of the total sample, however this concept is the basis for most valve-based modulators.

An appropriate example of valve-based modulator is shown on Figure 2.7. Initially (A) compounds leave the first column and enter a sample loop (also known as an “accumulation capillary”) and then (B) are flushed into the second column, much like the Deans switch setup. In this example, however, all the sample undergoes this process rather than just part of it. This is considered a “forward fill/flush” system as the flow direction for either the filling (A) or

flushing (B) phase is the same. This type of modulator is also known as differential flow modulator as the focusing effect of the modulator is due to the use of low flow rates in the first dimension and very high flow rates in the second dimension. Recently, Agilent introduced integrated microfluidic setups (named as CFT modulators) based on this principle to perform efficient GC×GC analyses with simple, user-friendly column connections.

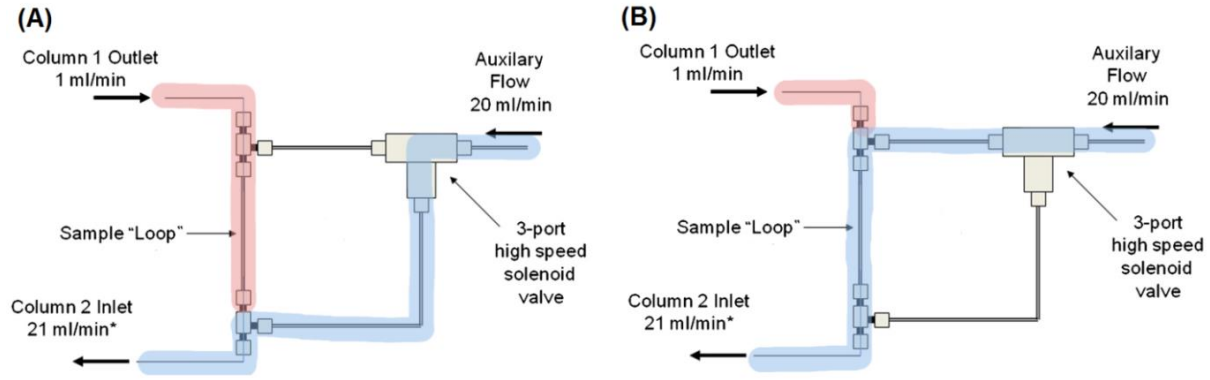


Figure 2.7 *– Forward fill/flush system (adapted from Griffith et al. 2012)*

The modulation system used in this project is slightly different from the one described above. This reverse fill/flush system is further discussed and analyzed in section **Erro! A origem da referência não foi encontrada.** of this report.

2.2.3 GC×GC method parameters

Gas chromatography, as an analytical tool, relies on the perfect synchronization of a large number of parameters and, as such, requires the analysis to be optimized for the sample in question and the desired separation. This might mean that separation does not need to be perfect for every compound if there is only one required compound or family, the operating conditions can be altered to sacrifice separation quality in other areas, as long as it favors the separation of the compounds that matter for the analysis in question. This process of parameter optimization is usually called "method development" and it's basically a trial-and-error process to create a tailor-made method for a specific purpose.

2.2.3.1 Oven temperature

While very early GC analysis were done with constant temperatures, analyzing gasoline matrices would either take too long at low temperatures as heavier compounds would take an extremely long time to elute, or lose resolution if high temperatures were used since lighter compounds would elute way too fast to be properly separated. Setting up an oven temperature program overcomes this obstacle of isothermal analysis. With an adequate temperature gradient, resolution can remain satisfactory for most of the compounds, while saving time in the overall analysis. Special care has to be taken when working with stationary phases that are

not able to withstand extreme temperatures, so as not to disable their separation capability or even permanently damage them.

2.2.3.2 Carrier gas flow rate and linear velocity

The flow rate of the carrier gas has an important effect on retention time and elution temperature. In accordance with the van Deemter equations, shown in Figure 2.8, there is an optimal linear velocity for the carrier gas of choice.

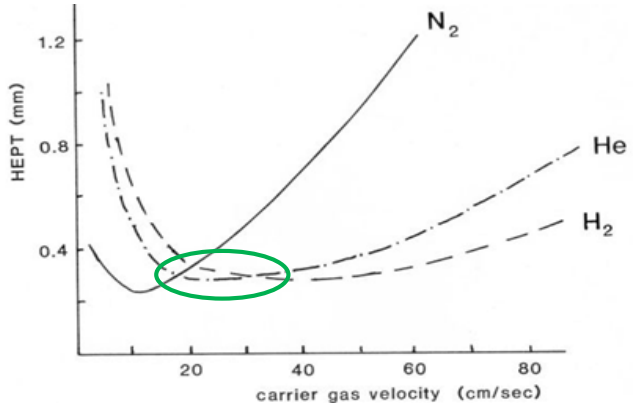


Figure 2.8 *– van Deemter equations for different possible carrier gas choices (optimal range linear velocity range shown in green for helium)*

This behavior is due to the viscosity of the different gases, and how it affects the diffusion of compounds in the mobile phase through the chromatographic column. To keep the linear velocity within the column at the optimal range, every time there is a change in column geometry (length, internal diameter and film thickness) the proper flow rate must be calculated. A higher flow rate has two main effects on elution: on one hand, it makes compounds elute faster through both columns which would intuitively mean a shorter retention time but since the compounds elute faster, the temperature at the time of elution through the second dimension is lower, which means that the compound will be more retained in the second column. These two effects counterbalance each other and this must be taken into account in the quest for optimal separation. Higher flow rates also promote thinner peaks rather than broad ones (Ong et al. 2002).

In GCxGC systems it is impossible to maintain column efficiency unless both columns have the same internal diameter. In the cryogenic system, if the second column has a smaller internal diameter than the first, the linear velocity will be drastically higher in the second dimension. The same happens in the second dimension of a differential-flow modulation system. Since compounds must be completely flushed from the accumulation capillary in a quick and efficient manner, the flow rates imposed by the auxiliary carrier gas are much higher than the optimal ones.

2.2.3.3 Modulation period

Modulation period is one of the most important parameters to take into account. It has a profound effect in the separation quality and the final results on the analysis. In the modulation process, compounds are sampled in order to be re-injected to the second dimension. If this sampling process is not quick enough, compounds that had been previously separated in the first dimension might be re-mixed in the modulator which negates the first column's selectivity and promotes co-elutions. This limits the time compounds have to elute through the second dimension, to a few seconds. Consequently, the modulation period, defined as time it takes for a modulator to complete one of its working cycles, is more or less equivalent to the maximum time a compound should take to elute through the second dimension.

Short modulation periods (a few seconds) increase the resolution of the first dimension separation but also increase the risk of wrap-around (compounds taking too long to traverse the second dimension and remaining in the column until the next fraction is injected into the second column). Longer modulation periods eliminate wrap-around and, since compounds are given more time to traverse the second column, it may help to increase second dimension separation with a suitable temperature program adjustment. However, if the modulation period is too long, the first dimension separation quality will suffer since compounds get mixed in the modulator's sampling phase.

2.2.3.4 Injection volume and split ratio

The volume of sample that is injected and the split ratio can affect the peak definition and it's similarity to a Gaussian distribution. Too much injected sample (and equivalently, a small split ratio) may cause saturation of the most intense peaks which makes quantification and MS identification harder and may increase peak tailing or fronting. On the other hand, if too little is injected, a lot of the compounds that are in the mixture at smaller concentrations may not even be detected.

2.2.4 Stationary phase configuration

Given the number of columns available on the market, there are practically limitless combinations of stationary phases. However, we can classify GC×GC configurations in two main classes. The first class of GC×GC configurations comprises a non-polar column followed by a polar column. This arrangement is called "normal" and is considered orthogonal since it allows a practically independent separation in each column: in the first dimension compounds are separated according to their volatility while the main factor in the second dimension is polarity, as the elution is considered isothermal due to its short duration. Orthogonality, in fact, is defined by the ability of the two separations to be uncorrelated, which means one would not affect the other. However, completely orthogonal systems are not realistically possible (Poole,

Poole 2008). Deliberately non-orthogonal configurations (polar in the first dimension and non-polar in the second dimension) are called “reverse” configurations and also produce interesting results. Polar compounds are highly retained in the first dimension which allows for greater resolution between compound families (Adahchour et al. 2004).

The structure of the typical chromatogram differs depending on whether a normal or reverse configuration is used, as is illustrated in Figure 2.9 for hydrocarbons families.

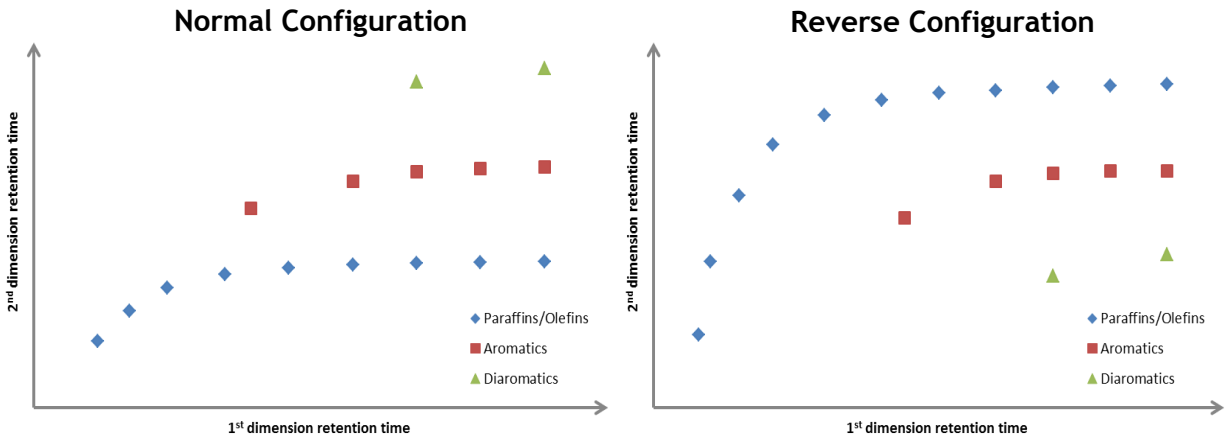


Figure 2.9 *– Retention behavior of different families in different configurations.*

In normal configurations, paraffins and olefins which are not very polar get poorly retained in the second dimension while aromatics are slightly more, followed then by diaromatics. Reverse configuration is not as straightforward since there are two retention mechanisms at work in the first dimension. Low polarity compounds such as paraffins and olefins are not as well retained now in the first dimension which means they arrive at the second column at low temperatures. This increases their retention time in the second dimension since the lower the temperature is, the more retention is achieved in non-polar columns. Aromatics are retained slightly better in the first dimension and, as such, enter the second column at higher temperatures, meaning that their retention time will be slightly decreased comparatively. The same but at a greater magnitude happens with diaromatics, making them even less retained in the second dimension (Omais et al. 2012).

Column geometry is also an important factor in separation. The length of the first column should be enough that first dimension resolution is acceptable but not so long that when the sample reaches the second column the oven temperature is too high and compounds elute too quickly, resulting in poor second dimension separation. The same principle is applicable to the second dimension length: columns should be long enough to provide good separation while not being so long that the least retained compounds from one modulation are able to catch up with the most retained compounds from the previous modulation, resulting in wrap-around.

Inner diameter and film thickness are the two other factors in column geometry and both have an influence on compound retention. Thick films are interesting regarding their ability to separate large amounts of compounds without saturation, resulting in long retention times, contrary to thin films. However, thicker film will also make the column more susceptible to degradation at higher temperature, thus increasing column bleeding (background signal due to the degradation of the stationary phase). Regarding internal diameters, wide-bore columns can be used with high carrier gas flow rates, while smaller internal diameters lead to higher efficiency. Depending on the type of modulators, some guidelines have to be followed when selecting column geometries.

2.2.5 Previous work on modulation comparison

As stated previously, GC×GC is nowadays used to analyze heavy cuts of petroleum products. Semard et al. (2011) have compared the results of a cryogenically modulated analysis of light cycle oil (the diesel cut from the FCC unit) with a valve-based modulation approach using an Agilent CFT microfluidic modulator with a forward fill/flush operation. Though the microfluidic system provided a worthwhile effort in terms of separation and an economical advantage due to the lack of use of cryogenic fluid, the cryogenic modulator used still showed superior resolution, comparatively.

Griffith et al. (2012) evaluated the performance of a reverse fill/flush modulator and compared it to an FFF system and found that there was an improvement in the focusing effect of the modulation, since results showed narrower peak widths and a decrease in signal tailing.

More recently, Duhamel et al. (2015) have done the same basic experiments but on vacuum gas oil – a heavier, more complex sample than light cycle oil – and a gamut of different valve-based modulation systems in both forward and reverse fill/flush operation. The study corroborated the results of Griffith et al. regarding RFF microfluidic modulation.

An internal IFPen technical note (Boiron, Souchon 2015) has further shown the feasibility of both cryogenic and microfluidic GC×GC modulation systems for diesel cut analysis, specifically using straight-run gas oil. The objective of the technical note was to characterize the operational process of the microfluidic modulator that was also used in the experiments done within the scope of this project. This technical note was, thus, an essential foundation for the project at hand, providing excellent information about the functioning of the modulator in question.

3 Experimental Section

The project was developed using two GC×GC setups, each with a different modulator type. The GC×GC with the cryogenic modulator was coupled to both FID and MS detectors. The mass spectrometer enabled the identification of the eluted compounds. Figure 3.1 shows the basic diagram of the cryogenic setup.

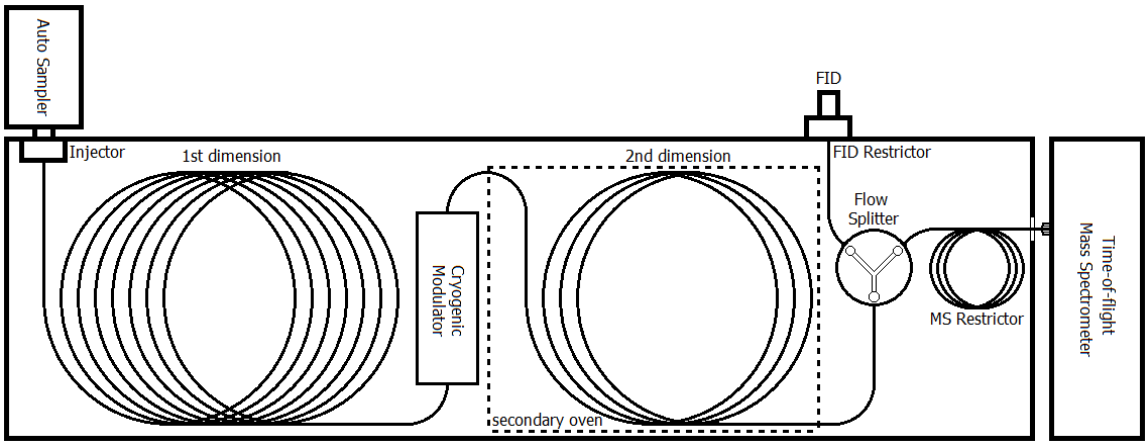


Figure 3.1 *– Schematic illustration of the cryogenic GC×GC setup*

The instrument used was the LECO Pegasus 4D GC×GC-TOFMS which incorporates a time-of-flight mass spectrometer as a default detector along with the FID. The automatic liquid sampler is an Agilent 7683B and the chromatograph is an Agilent 6890N. ChromaTOF was the software that came with the LECO and it was used on-line to control the GC×GC apparatus (creation of analysis methods and sequences) and for the preliminary assessment of the success of the method and separation quality. Of note is the fact that the chromatograph includes a secondary oven just above the modulator, which was used in some experiments.

Figure 3.2 illustrates the operation of the LECO cryogenic modulator. The system used in the experiments is a dual-stage quad-jet cryogenic modulator that works by means of the same principle as the CO_2 modulator referenced earlier but this time using two cold nitrogen jets. The jets are cooled with liquid nitrogen. The use of cold nitrogen rather than CO_2 allows for a more efficient trapping of very light compounds present in gasolines. It also introduces two hot air jets which much more rapidly re-inject of compounds into the second dimension, thus,

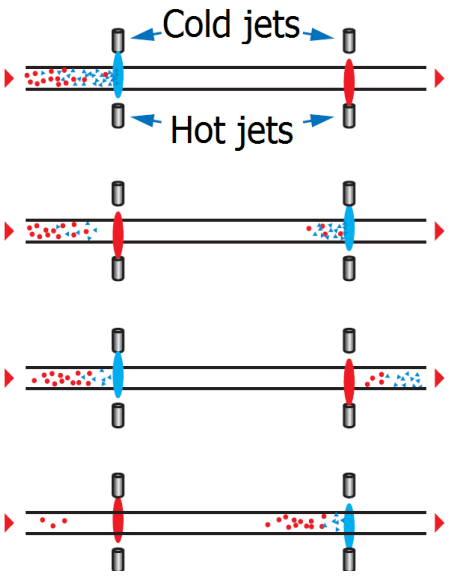


Figure 3.2 *– Modulation with a quad-jet cryogenic modulator (adapted from Fernandez et al. 2011)*

improving the focusing effect on the modulated compounds which ends up reducing peak tailing. The timing of the jets can be adjusted to optimize the focusing action but a ratio of 3:1 cold-to-hot was used throughout the project.

In Figure 3.1, a flow splitter is represented at the end of the second column. A flow splitter was indeed used at the start of the experiments as to test the viability of simultaneous detection with both the FID and the MS. A number of different flow splitters were tested and the results of these experiments are presented in section 4.1.1. From the flow splitter, two restrictors connect the second dimension to both detectors. The restrictor lengths were calculated using HP FlowCalc 2.0 so as to have a pressure at the splitter slightly above the atmospheric pressure and to achieve the same flow rate in both sides of the splitter. As shown in Figure 3.1, the MS restrictor had to be of greater length than the FID restrictor since the mass spectrometer is under vacuum (approx. 1×10^{-7} torr).

Having the knowledge of which stationary phases are the most effective to obtain the desired separation and optimizing the analysis conditions on the cryogenic setup, the following experiments focused on translating those optimized conditions to the microfluidic. A diagram of the microfluidic setup is shown in Figure 3.3.

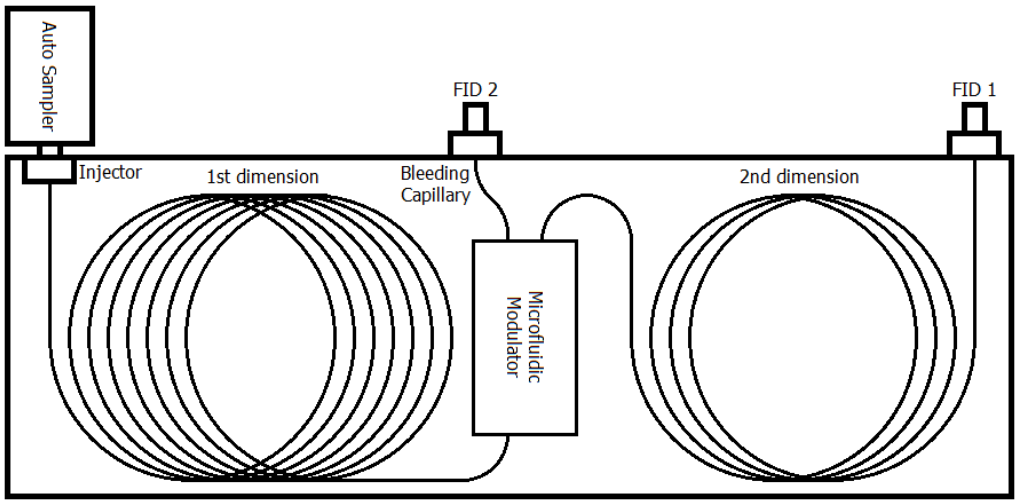


Figure 3.3 *– Schematic illustration of the microfluidic GC×GC setup*

The gas chromatograph is an Agilent 7890B with an Agilent 7693A auto sampler. The software Open Lab Chemstation was used for on-line control and initial data analysis. This setup is a lot simpler than the cryogenic one since it has no secondary oven, no flow splitter and only has one detector choice even though there are two FID's rather than one. The two detectors are necessary due to the operating procedure of the modulator. The modulation system used in the presented setup was described by Griffith et al. (2012). Its functioning loop is illustrated in Figure 3.4.

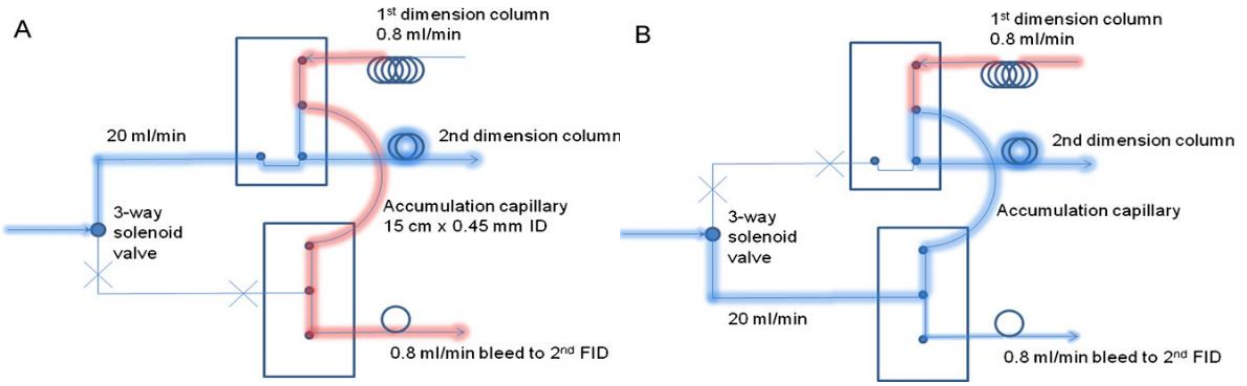


Figure 3.4 *– Microfluidic modulator functioning steps: (A) fill; (B) flush (Griffith et al. 2012)*

At first (A), an accumulation capillary (15 cm length, 0.53 mm internal diameter, inert fused silica tubing) is filled with the eluted compounds from the first dimension. After this (B) the capillary is flushed by the carrier gas coming from the 3-way solenoid valve into the second column. It builds on previous valve-based modulators by using a reverse fill/flush method, where the carrier gas flushes the accumulation capillary in the opposite direction to how the modulated sample entered, as opposed to a forward fill/flush where the fill and flush directions are the same. This has the advantage of largely reducing second dimension tailing. It is obviously much cheaper to run experiments on a GC×GC that uses microfluidic modulation since it does not require cryogenic fluid or the kind of infrastructure associated with its use.

The modulator has one possible inlet for the mobile phase but two possible outlets: one of leads the compounds through the second column and into FID 1, identical to any other GC×GC system. The other outlet goes through what is called a bleeding capillary, into FID 2. The purpose of this capillary is to provide an outlet for the carrier gas coming from the first dimension which passes through the accumulation capillary during the fill cycle (Griffith et al. 2012). To make sure that no compounds should be detected in FID 2 three conditions must be met: firstly, one must make sure that the bleed capillary has the correct dimensions in order to make sure that both the flow rate in the bleed capillary is the same than the 1D flow rate (which is easily done using HP FlowCalc 2.0); secondly, the fill and flush times must be carefully adjusted so that there is an minimum ratio of 1.5 flushed volume over fill volume (Boiron, Souchon 2015), which assures that all the compounds that entered the accumulation capillary get flushed into the second column; finally, it is important that there is no overfilling of the accumulation capillary, which would cause a substantial loss of sample as well as inefficiency in the modulation. An example of the calculations necessary to assure that the last two conditions are met is included in Appendix 1.

The analytical conditions and column combinations tested are described along with the results in Chapter 4.

4 Results and Discussion

The sample used to optimize the separating conditions was an effluent of an FCC process and will be henceforth referred to as “S8244”.

4.1 Cryogenic Setup

The first tests were undertaken in the cryogenic setup because the optimization of operating conditions is more simple and straightforward than the microfluidic. This is true because altering the modulation period in the cryogenic setup has little to no effect on separation, as opposed to the microfluidic system, where, besides the modulation period, the re-injection time in the second dimension must be altered which may cause differences in the retention behavior of some compounds. As long as the ratio of cold versus hot jet timing is kept somewhat consistent, no changes in second dimension retention behavior are to be expected, though, first dimension separation will not be as effective with higher modulation periods as re-mixing of compounds might happen in the modulator.

4.1.1 Flow splitter tests

As referenced previously, experiments were made with a flow splitter at the end of the second column. The objective of its use was to enable simultaneous detection between the FID and MS, which would not only shorten the analysis time – one less analysis to make and lack of time wasted on the laborious and sluggish setup required for the MS - but would also prevent possible differences in retention times between the FID and MS analysis. In order to correctly split the flow, two restrictors made out of inert fused silica capillaries were used to allow the compounds to elute to both the FID and the MS.

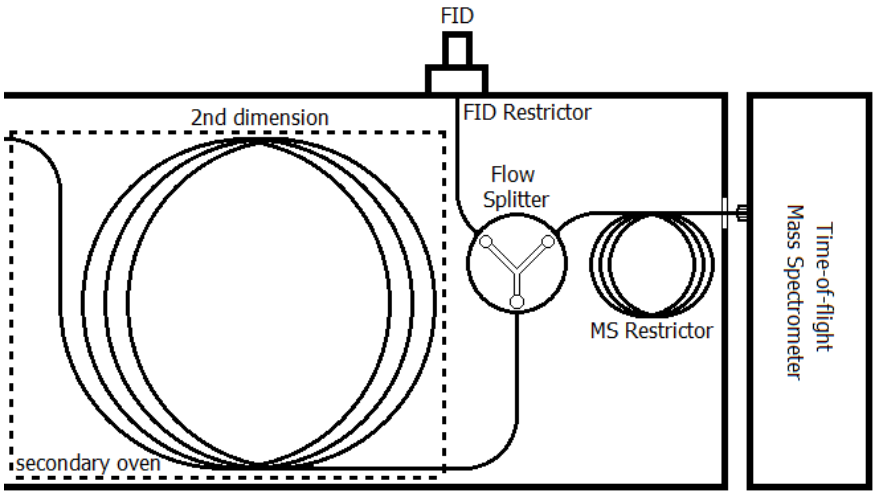


Figure 4.1 *– Flow splitter feeding both detectors simultaneously*

Four different column connectors were tested. The first splitter tested was the Restek Universal "Y" Press-Tight Connector made of fused silica glass. In the first few tests, the Restek "Y" performed quite well, providing the appropriate flow rates to each detector with minimal influence on the chromatographic results. However, in subsequent analysis, the heating cycles used in the chromatograph oven would make the glass contract and expand, which caused severe leaks and therefore, has led to a decrease in the signal-to-noise ratio, especially in the MS and imperfect separations. In order to avoid the leaking problem, a different splitter was tested – the SGE SilFlow microfluidic splitter. The SilFlow splitter managed to diminish the leaks observed in with the repeated use of the Restek "Y", however it introduced a different problem: peak tailing in the second dimension. This tailing is most likely an effect of the presence of dead volumes within the column-splitter connections and within the splitter itself and this effect greatly impacts the separation quality, producing unacceptable results. A different microfluidic splitter was then tested to try and eliminate the tailing problem. The Agilent CFT (Capillary Flow Technology) 2-way splitter results show slight improvement over the SilFlow splitter, however, peak tailing is still quite prevalent in the chromatogram, which, again makes this option non-viable. Finally, to verify whether the problem was, in fact, coming from the dead volumes in the splitters' connections, the Agilent CFT Union, which shares the type of connection present in the CFT splitter, was also tested. The results obtained with the CFT Union are again marginally better than those of the SilFlow splitter but still not ideal, thus confirming the source of the tailing peaks. All the tests were done with the exact same conditions.

In Table 4.1, the performances of each splitter have been compared to the signal obtained in a typical analysis where the second column is connected directly into the FID. To make the tailing more evident, the portion of the chromatogram shown is a section which contains very intense peaks, namely toluene, ethylbenzene, m-xylene and p-xylene (usually co-eluted), o-Xylene and isopropylbenzene.

To adequately quantify the peak tailing, the isopropylbenzene peak was chosen to calculate the Tailing Factor which basically measures the deviation of the shape of the peak from a Gaussian distribution. The isopropylbenzene peak was selected since it is not as intense as the other peaks that were shown, which means that there is no risk of phase saturation. Having a saturated peak would skew the results because phase saturation causes peak fronting, the reverse phenomenon to peak tailing. Figure 4.2 explains the

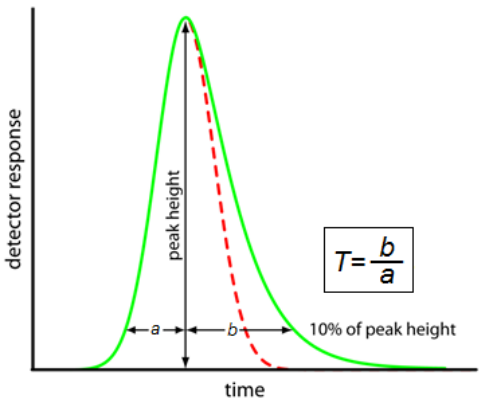


Figure 4.2 *– Calculation of the Tailing Factor - T*

necessary calculation to determine the Tailing Factor and the results of this calculation are presented in Table 4.2.

Table 4.1 *– Flow splitter test results*

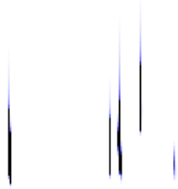
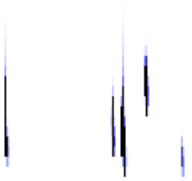
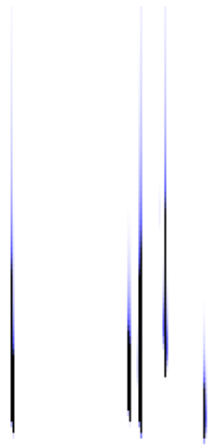
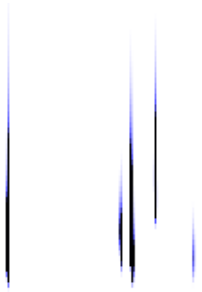
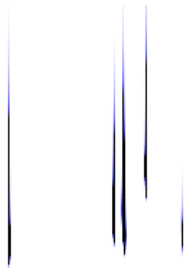
FID (control)	Restek Glass "Y"	SGE SilFlow Splitter	Agilent CFT Splitter	Agilent CFT Union
Compounds (left to right): • Toluene • Ethylbenzene • m-/p-Xylene • o-Xylene • Isopropylbenzene				
				

Table 4.2 *– Tailing Factor calculation results*

	FID	Restek "Y"	SilFlow	CFT Splitter	CFT Union
Peak Height	2598	814	2667	764	1534
Retention Time (min)	42.3180	43.8327	42.8333	42.5810	43.1622
10% Peak Height	259.8	81.4	266.7	76.4	153.4
a (min)	0.0013	0.0012	0.0011	0.0018	0.0016
b (min)	0.0016	0.0023	0.0047	0.0040	0.0042
Tailing Factor - *T*	**1.231**	**1.917**	**4.273**	**2.222**	**2.625**

For an ideal Gaussian peak, *T* would be 1. However, peaks are still considered almost symmetric with values of *T* between 0.5 and 2. The FID peak, as expected, fits this criterion. The Restek "Y" is also adequately approximated to a symmetric peak, however, it is not viable due to the leaks that happen in later analysis. All the other splitting methods fail to keep the peaks within the tailing factor limits. The fact that a proper solution was not found meant that simultaneous detection would not be attempted. The method parameters for the different column configurations would be optimized using the FID and after the fact, the best configuration would then be selected and connected to the MS for identification analyses.

4.1.2 Normal configuration

In the initial stages of the method development, a few assumptions were made to narrow down column selection: both first and second dimension columns should function while at low temperatures in order to improve the separation of the more volatile compounds; the first dimension column would be a non-polar column with dimethylpolysiloxane as the stationary phase composition due to their proven ability to separate compounds by volatility (dimethylpolysiloxane columns are used in several standard methods at IFPen as well as ATSM standard D6733); the second dimension column should be of a smaller diameter than the first in order to increase the linear velocity of the mobile phase, thus allowing for short modulation periods and fast separation; finally, the second dimension column selection should cover a large range of polarity – from mid-polar to very highly polar stationary phases. Buying a large number of different columns would be very expensive, so restrictions concerning column availability at the IFPEN GC laboratory was also a factor. Using these assertions, a variety of column configurations was selected and can be viewed in Table 4.3.

Table 4.3 *– Stationary phases used in the cryogenic normal configuration tests*

	1st dimension	**2nd dimension**	
	Manufacturer/product name length; internal diameter; film thickness Temperature limits	Manufacturer/product name length; internal diameter; film thickness Temperature limits	Active groups in stationary phase (Retention mechanism)
(A1)	Agilent J&W HP-PONA 50 m; 0.2 mm; 0.5 µm [-60 °C : 350 °C]	Restek Rtx-1701 1.5 m; 0.1 mm; 0.1 µm [-20 °C : 280 °C]	14% cyanopropylphenyl (Mid-polar)
(A2)	Agilent J&W HP-PONA 20 m; 0.2 mm; 0.5 µm [-60 °C : 350 °C]	Restek Rtx-1701 1.5 m; 0.1 mm; 0.1 µm [-20 °C : 280 °C]	14% cyanopropylphenyl (Mid-polar)
(A3)	Agilent J&W HP-PONA 20 m; 0.2 mm; 0.5 µm [-60 °C : 350 °C]	Restek Rtx-200 1.5 m; 0.1 mm; 0.1 µm [-20 °C : 340 °C]	Trifluoropropyl (Mid-polar)
(A4)	Agilent J&W HP-PONA 20 m; 0.2 mm; 0.5 µm [-60 °C : 350 °C]	Agilent J&W DB-Wax 1.5 m; 0.1 mm; 0.1 µm [20 °C : 250 °C]	Polyethyleneglycol (Highly polar)
(A5)	Agilent J&W HP-PONA 20 m; 0.2 mm; 0.5 µm [-60 °C : 350 °C]	Supelco Beta-Dex 120 1.5 m; 0.1 mm; 0.1 µm [30 °C : 230 °C]	20% ß-cyclodextrin (Chiral)
(A6)	Agilent J&W HP-PONA 20 m; 0.2 mm; 0.5 µm [-60 °C : 350 °C]	SGE BPX70 1.5 m; 0.1 mm; 0.1 µm [50 °C : 260 °C]	70% Cyanopropyl (Very highly polar)

The 50 meters HP-PONA column was chosen for configuration (A1) solely because there is a pre-existing method at IFPEN which uses that column for detailed hydrocarbon analysis of gasolines, thus making it a good starting point for the project. For the second dimension a common mid-polar column was necessary, therefore, the Rtx-1701 was selected. Several analysis with different method parameters were made, though, for the sake of brevity, only the optimized method for each configuration will be in the main section of this paper. The optimized method for configuration (A1) are presented in Table 4.4 and the resulting chromatogram, obtained using the 2DChrom software, is shown in Figure 4.3.

Table 4.4 *– Optimized operating conditions using configuration (A1)*

Injection	Split/Splitless Inlet; 250 °C; 1:200 Split Ratio; 1 µl
Carrier Gas	Helium; 1 ml/min
Oven Program	-20 °C (0.2 min) → 2 °C/min → 250 °C (0.2 min)
Modulation	4 s (0.5 s hot jet; 1.5 s cold jet)
FID	300 °C; 100 Hz; H_2 - 40 ml/min; Air – 400 ml/min; He (make-up) - 25 ml/min

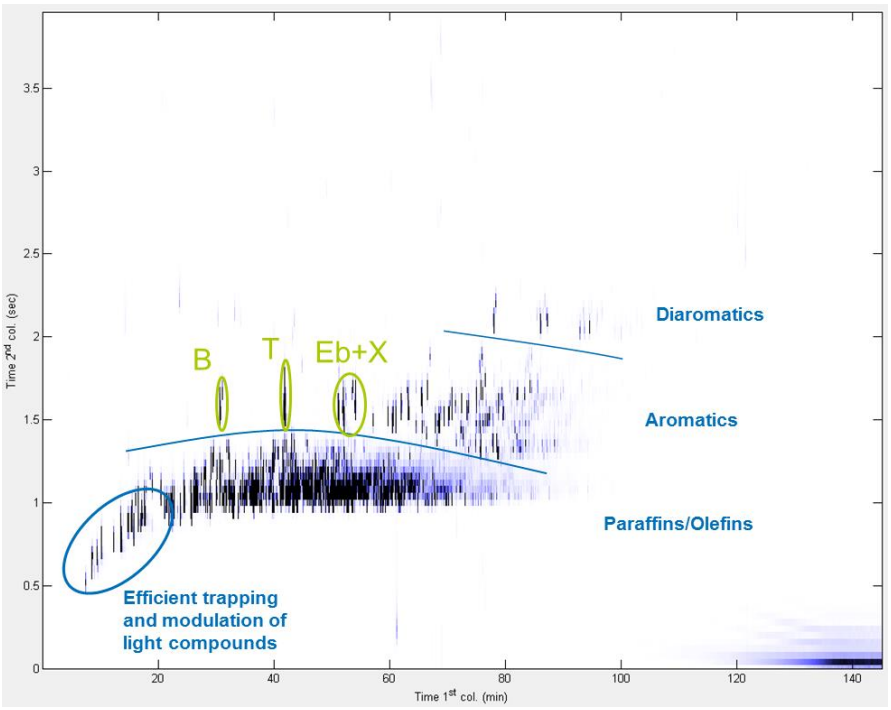


Figure 4.3 *– Optimized chromatogram obtained in configuration (A1); B – Benzene; T – Toluene; Eb – Ethylbenzene; X - Xylenes*

Configuration (A1) proved to be good enough to separate the different compound families (paraffins, olefins and aromatics) from each other, which makes this an adequate separation. Also visible is the fact that the cryogenic modulator was able to successfully modulate the light compounds due to the use of liquid nitrogen as the cryogenic fluid. This analysis is, however, not ideal. Some of the more concentrated compounds such as toluene and the xylenes are saturating the stationary phase of the second column, as shown in Figure 4.4. This could be

remedied by having a lower volume on sample injected into the column, as well as a higher split ratio, in order to have a smaller quantity of products entering the column. More importantly, compounds are not very well separated in the second dimension, taking less than 2 seconds from the least to the most retained compounds. This happens because the first column is 50 meters long (the length required in the IFP0104 or ASTM D6733 standard) which means that compounds take a very long time to reach the end of the first column. At the time compounds reach the end of the first column, the temperatures in the oven are already too high for compounds to be properly retained in the second column. This means that the separation could be improved by reducing the length of the first column, therefore, configuration (A2) includes a shorter first dimension of 20 meters rather than 50. This increase in second dimension separation also meant that the modulation period had to be raised from 4 to 5 seconds.

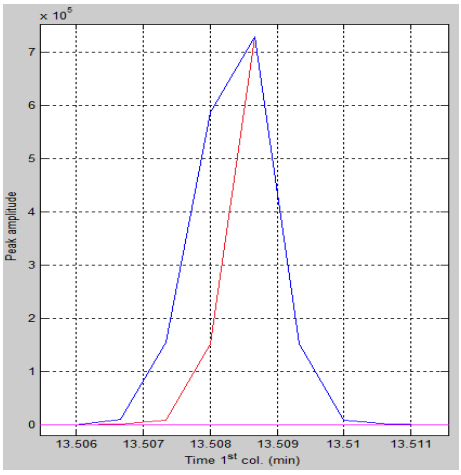


Figure 4.4 *– Example of a fronting peak in configuration (A1); in blue: real signal; in red: Gaussian peak*

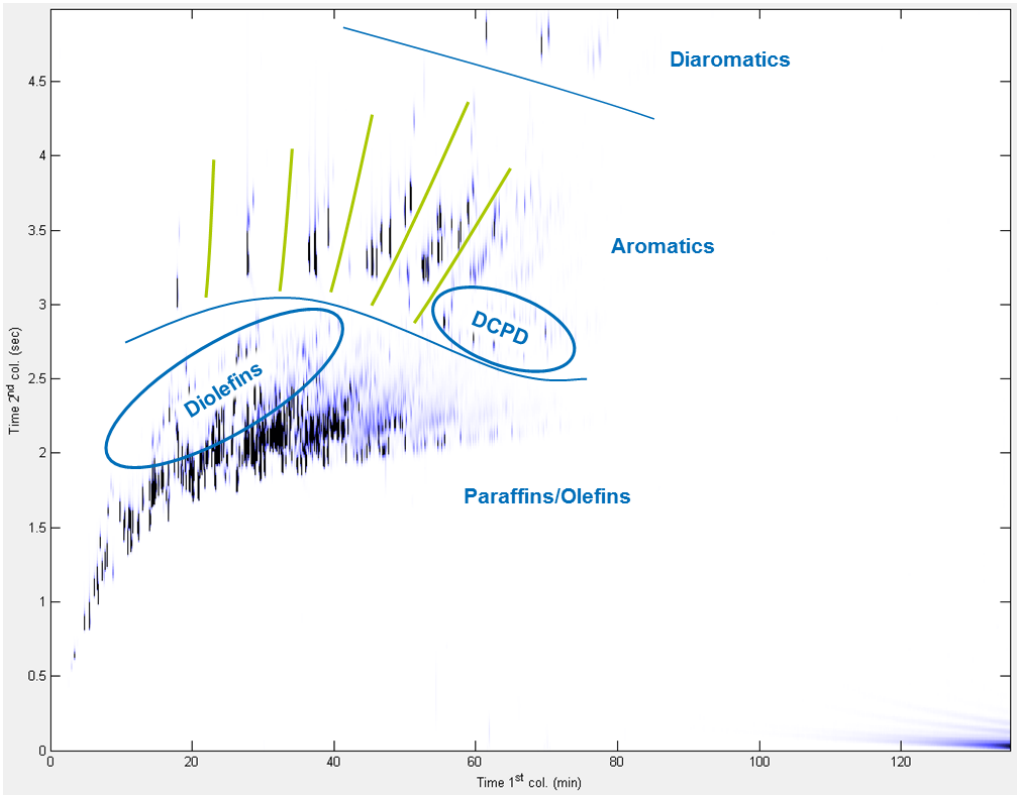


Figure 4.5 *– Optimized chromatogram obtained in configuration (A2)*

Using configuration (A2), the resulting chromatogram presents a clearly visible improvement over the first configuration. Peaks are clear and sharp, compounds are well modulated and very well separated. Of worthy note is the pronounced separation of diolefins from the main

paraffins and olefins region and the detached dicyclopentadiene (DCPD) region right next to the aromatics. Finally, there is a good roof-tiling effect present in the aromatics section, separating aromatics of different molecular weight and number of carbon atoms.

Coming off configuration (A2), it is hard to expect a better separation from any of the other stationary phase configurations. Configuration (A3) changes the second dimension stationary phase from the 14% cyanopropylphenyl active groups to trifluoropropyl groups. This column – the Restek Rtx-200 - is still a mid-polarity phase, however, it has a slightly different retention mechanism than the Restek Rtx-1701. The resulting chromatogram from the optimized conditions of configuration (A3) is present in Figure 4.6.

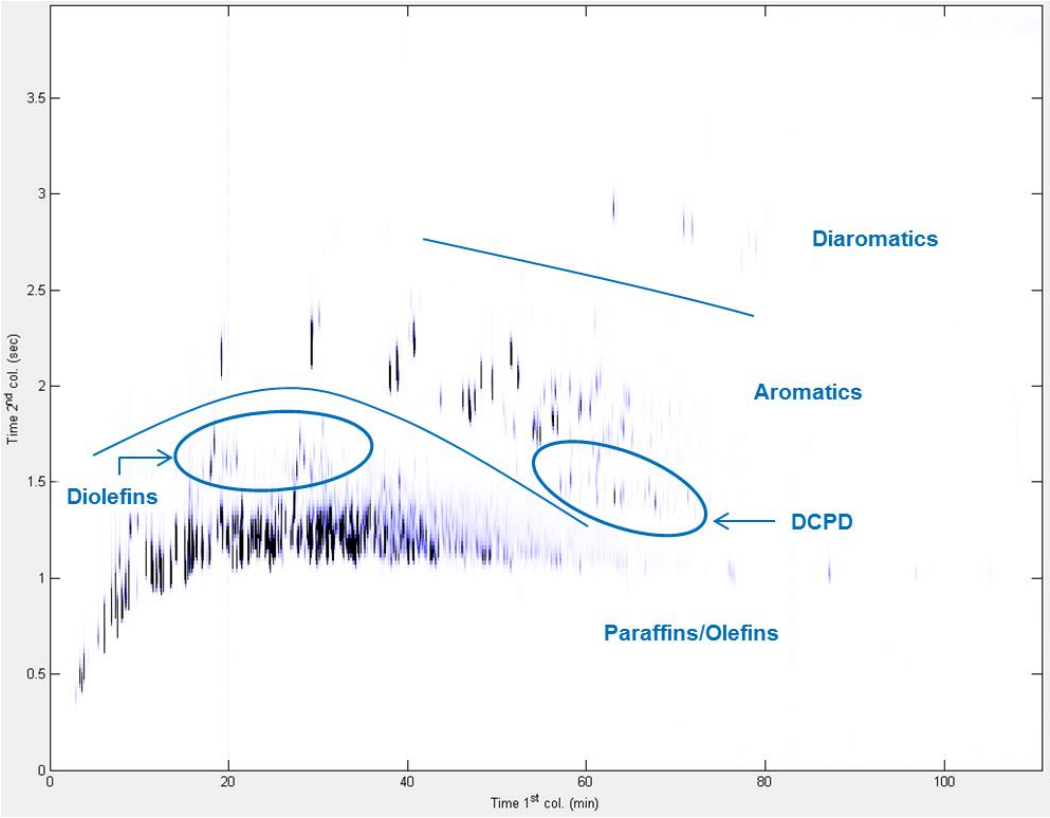


Figure 4.6 *– Optimized chromatogram obtained in configuration (A3)*

Due to the fact that the Rtx-200 phase is not as retentive as the Rtx-1701, the optimal modulation period for configuration (A3) can be shortened from 5 seconds to 4 seconds. This lack of retention is especially evident at higher temperatures, where the compounds have a comparatively shorter retention time in the second dimension, than in configuration (A2). Configuration (A3) still has positive aspects to its separation, though. There are still some diolefins which are properly separated from the remaining paraffins and olefins. The DCPD's are also still easily distinguished from the aromatics. Configuration (A3) is not as good as (A2), however it is still adequate.

Up until this point, all the columns tested had a minimum working temperature of at least -20 °C, and so, the same temperature program was used for all three of those configurations. Configuration (A4) tests a more polar second column than the one used in the previous tests – the DB-Wax, whose stationary phase is made of polyethyleneglycol. Unfortunately, this stationary phase has a minimum working temperature of 20 °C which forced a change in the oven temperature program. This is where the cryogenic setup's integrated secondary oven comes into play. Since the first column is still the HP-PONA, the main oven can remain at relatively lower temperatures while the second column can avoid being below of its minimal usable temperature by staying in the secondary oven which can be programmed to have a completely different temperature ramp.

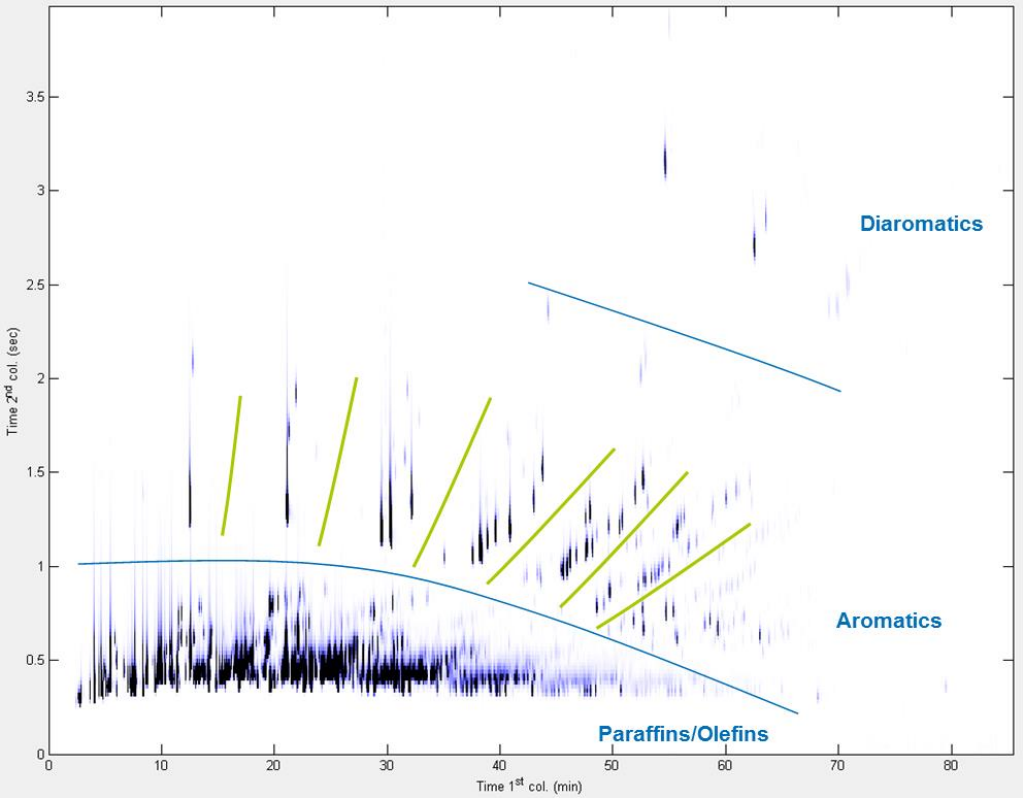


Figure 4.7 *– Optimized chromatogram obtained in configuration (A4)*

The particular analysis shown in Figure 4.7 was obtained using different temperature ramps in the first and secondary oven. Previous analysis with the DB-Wax phase had some disruptive wrap-around of the diaromatics which meant that this family of compounds was being excessively retained, even at the high working temperatures required by this stationary phase. The graph in Figure 4.8 represents the detailed oven temperature ramps optimized for configuration (A4). Regarding the separation quality, the polyethyleneglycol phase is more selective when it comes to the aromatics and diaromatics, rather than the less polar compounds like paraffins and olefins. Even though these last two families are not well separated, there is still some value to the separation, especially if the objective of the analysis is to titrate and

identify aromatics since there is an excellent roof-tiling effect in this zone of the chromatogram. Of course, when looking for an all-purpose analysis method, configuration (A4) is not ideal, and thus still does not surpass the practicality and convenience of configuration (A2). There is another negative to the DB-Wax results and this is peak tailing in the second dimension. In the paraffinic/olefinic compounds that are less retained in the first dimension, there is some visible second dimension tailing, as well as on the more concentrated aromatics like toluene and the xylenes. The reason for this phenomenon is the existence of a section of the second dimension that is out of the secondary oven which then connects to the FID. The presence of this cold spot in the flow path causes the compounds to be slightly more retained than they should in this particular section of the column, thus causing the peak tailing. However this is only a small problem and does not affect the separation quality in a very extreme way.

Figure 4.8 *– Oven programming ramps for the optimized analysis in configuration (A4)*

In configuration (A5), however, the peak tailing has a much more profound effect on the separation, as evidenced in Figure 4.9.

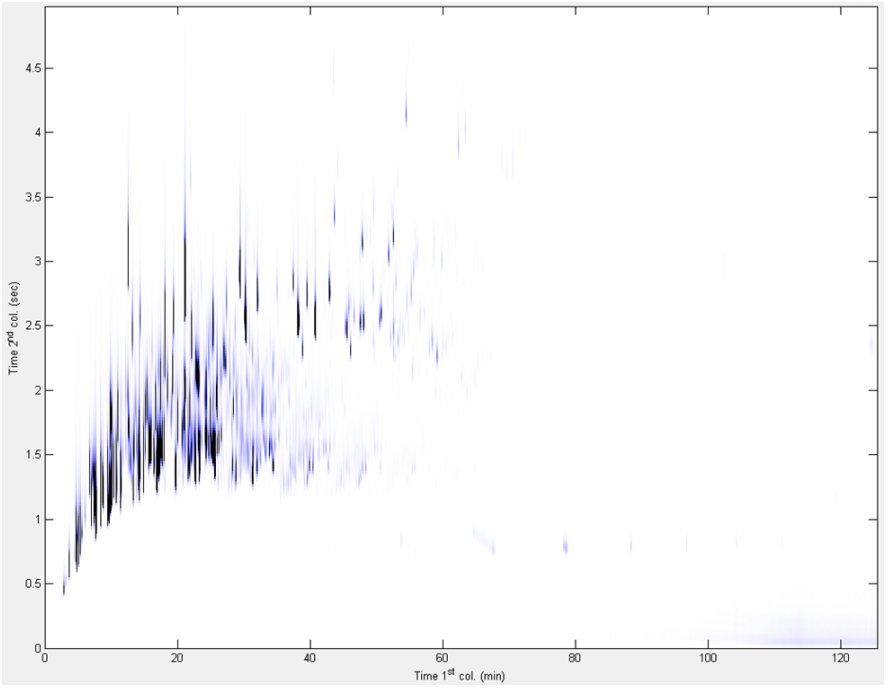


Figure 4.9 *– Chromatogram obtained in configuration (A5)*

The Beta-dextrine 120 column used as a second dimension has a minimum working temperature of 30 °C which means the cold spot will have an even worse impact on peak tailing than before

since the temperature difference from the main to the secondary oven will be bigger than the one used in configuration (A4). Both ovens share the same temperature ramp (increasing at a rate of 2 °C/min) however now the main oven starts at 0 °C and the secondary oven starts at 30 °C. This causes tailing so severe that there is no clear distinction between the different compound families. Configuration (A5) is, therefore, not suitable for the analysis of gasolines due to the fact that it is not able to work at the appropriate temperatures.

As a last try with highly polar phases, the SGE BPX70 was the last second dimension stationary phase attempted in the normal configuration (A6). Seeing as the minimum working temperature for this highly polar phase is 50 °C, the results presented in Figure 4.10 are unsurprisingly not very interesting.

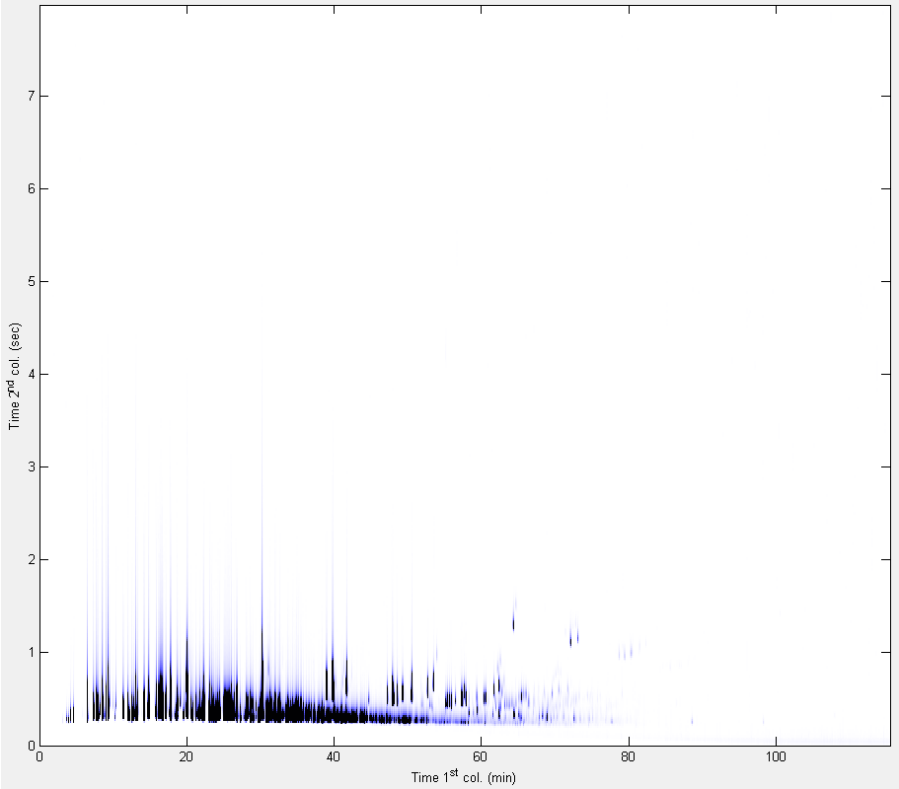


Figure 4.10 *– Chromatogram obtained in configuration (A6)*

The fact that the secondary oven starts at very high temperatures, means that compounds will elute very quickly through the second dimension, despite its high polarity. Heavier fractions of petroleum based products might be more adequately separated, however, as it stands, the BPX70 column is simply not appropriate for the analysis of light petroleum products such as gasolines.

4.1.3 Reverse configuration

As on the normal configuration, stationary phase configurations were chosen according to a few basic criteria. Availability was, again, taken into account, as there is a limited selection of columns accessible in the laboratory. A different range of retention mechanisms was chosen,

as well as columns able to handle low temperatures. As mentioned before, the second column should be of a smaller internal diameter than the first in order for the compounds to elute at higher linear velocities through the second dimension, thus decreasing the necessary modulation period. The second column is now the non-polar dimethylpolysiloxane phase since we are now working in reverse configuration, therefore, the Agilent J&W DB-1 (0.1 mm internal diameter, 0.1 µm film thickness) is a suitable choice since it has the appropriate dimensions to be used as a second column. The assortment of chosen columns is presented in Table 4.5.

Table 4.5 *– Stationary phases used in the cryogenic reverse configuration tests*

	1st dimension		2nd dimension
	Manufacturer/product name length; internal diameter; film thickness Temperature limits	Active groups in stationary phase (Retention mechanism)	Manufacturer/product name length; internal diameter; film thickness Temperature limits
(B1)	Agilent J&W VF-1701 Pesticides/MS 30 m; 0.25 mm; 0.25 µm [-20 °C : 300 °C]	14% cyanopropylphenyl (Mid-polar)	Agilent J&W DB-1 1.5 m; 0.1 mm; 0.1 µm [-60 °C : 350 °C]
(B2)	Restek Rtx-200 MS 20 m; 0.25 mm; 0.25 µm [-20 °C : 340 °C]	Trifluoropropyl (Mid-polar)	Agilent J&W DB-1 1.5 m; 0.1 mm; 0.1 µm [-60 °C : 350 °C]
(B3)	Restek Rtx-2330 25 m; 0.25 mm; 0.5 µm [0 °C : 275 °C]	Biscyanopropyl cyanopropylphenyl (Very highly polar)	Agilent J&W DB-1 1.5 m; 0.1 mm; 0.1 µm [-60 °C : 350 °C]
(B4)	DB-Wax 30 m; 0.32 mm; 0.25 µm [20 °C : 250 °C]	Polyethyleneglycol (Highly polar)	Agilent J&W DB-1 1.5 m; 0.1 mm; 0.1 µm [-60 °C : 350 °C]

The first configuration – configuration (B1) – makes use of the same stationary phases which produced the best results in the normal configuration tests, though, with a different geometry and a different manufacturer. The optimization conditions for the reverse configuration (B1) are shown in Table 4.6.

Table 4.6 *– Optimized operating conditions using configuration (B1)*

Injection	Split/Splitless Inlet; 250 °C; 1:500 Split Ratio; 0.1 µl
Carrier Gas	Helium; 1.2 ml/min
Oven Program	-20 °C (0.2 min) → 2 °C/min → 250 °C (0.2 min)
Modulation	5 s (0.63 s hot jet; 1.87 s cold jet)
FID	300 °C; 100 Hz; H_2 - 40 ml/min; Air – 400 ml/min; He (make-up) - 25 ml/min

These parameters were much easier to obtain now that the results from the normal configuration are available and a lot of them remain the same since they have been already optimized in those tests and are consistently producing good results or changing them does not have a large effect on separation (such as injected volume, split ratio). Figure 4.11 presents the results from the optimization of the conditions for configuration (B1).

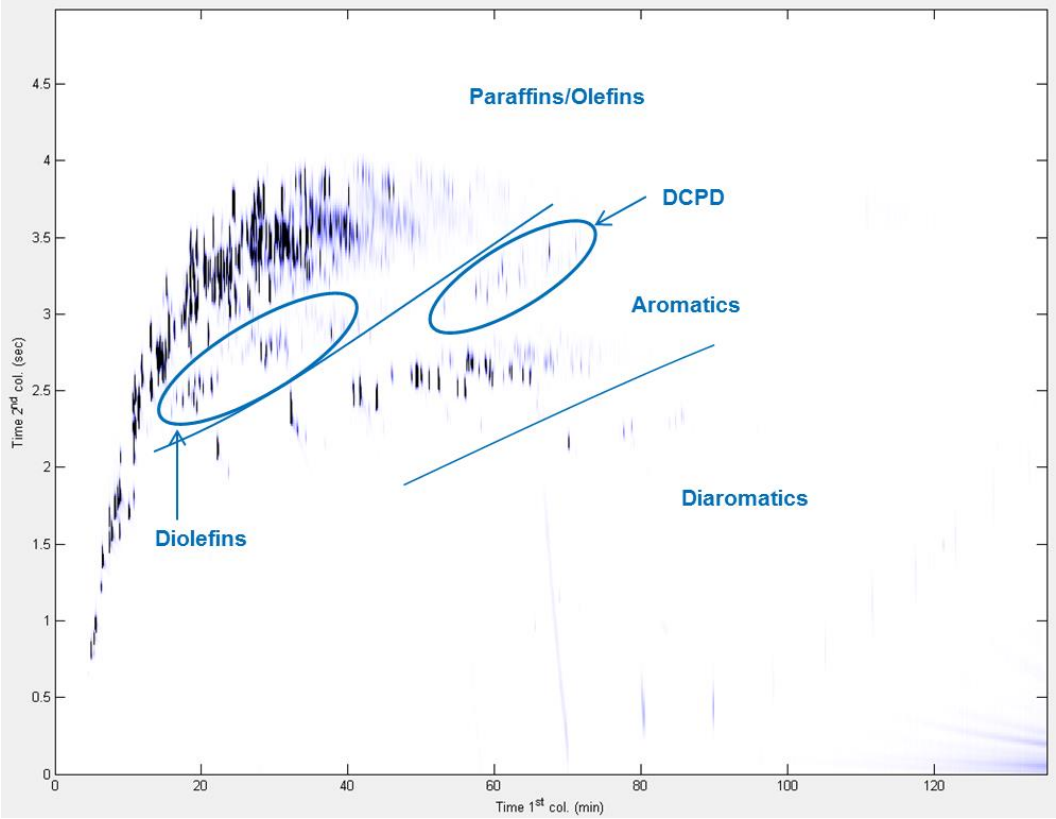


Figure 4.11 *– Optimized chromatogram obtained in configuration (B1)*

Once again, the 14% cyanopropylphenyl group stationary phase proves outstanding in the separation of most compounds present within the gasoline mixture. Since they are not very polar, the paraffins and olefins are not retained on the first dimension as with a completely non-polar column. This fact causes them to reach the end of the first column at low temperatures which, in turn, increases their second dimension retention time. This creates the typical structure associated with chromatograms from analyses done in reverse configuration with non-polar compounds at the top of the 2D chromatogram and polar compounds at the bottom. The information this kind of chromatogram gives is mostly complementary to the results obtained with the normal configuration: now there is a better second dimension separation inside the paraffins and olefins section rather than the aromatics. These last compounds are still adequately separated, however, with a clear distinction being visible between aromatics and DCPD's as well as a visible, although less pronounced, roof-tiling effect. The separation of diolefins from the main group of paraffins and olefins is also apparent, as it

was in configurations (A2) and (A3). In summary, configuration (B1) achieves the proper separation requirements for a gasoline analysis.

Configuration (B2) once again uses the Rtx-200 phase but this time as the first dimension, rather than the second. Figure 4.12 illustrates the results obtained from this configuration.

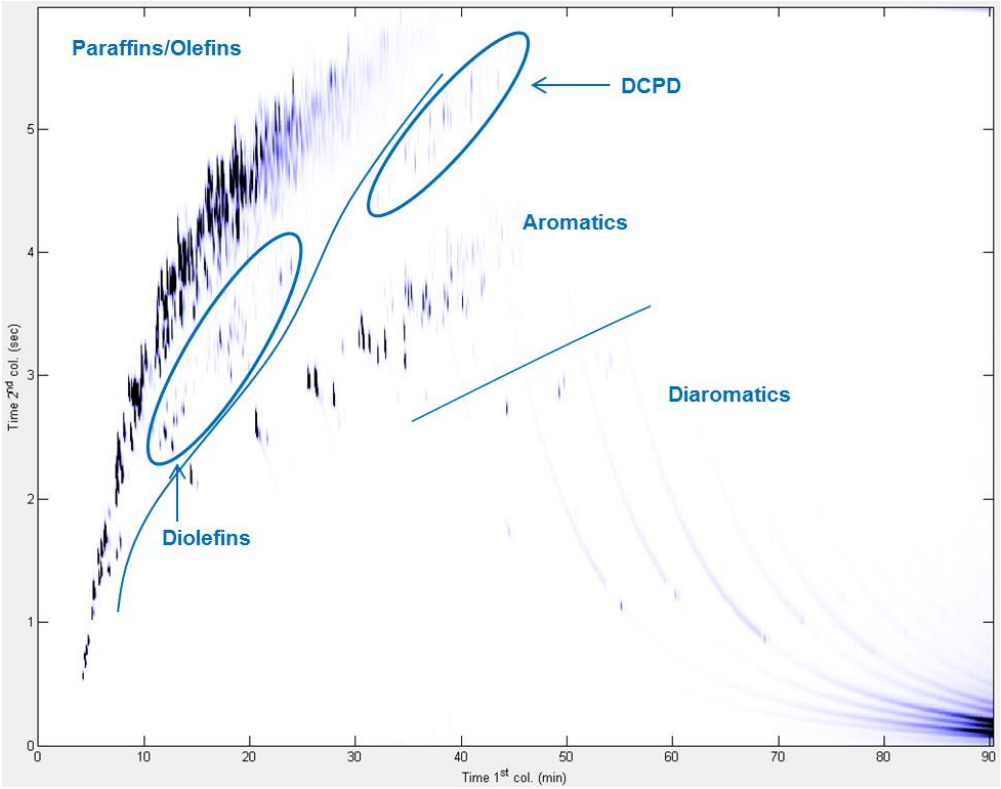


Figure 4.12 *– Optimized chromatogram obtained in configuration (B2)*

Again, the trifluoropropyl phase falls short of the 14% cyanopropylphenyl phase in terms of overall separation quality. The fact that the diolefins and DCPD's are adequately separated is promising, however as seen before, the Rtx-200 columns start to lose their retention ability as temperatures increase, leading to a loss of selectivity. This is what causes the chromatogram to seem like it is tilted upwards: the higher the temperature goes, the less retained the compounds are in the first dimension, meaning they arrive at the second dimension at lower temperatures than they normally would, thus resulting in more retention in the second column. The same happened in the normal configuration tests, just with the opposite effect since the Rtx-200 column was in the second dimension rather than the first. This decrease in retention forced the modulation period from 5 seconds to 6 and also an increase in the temperature rate from 2 °C/min to 3 °C/min which even further reduces the quality of the separation, with this reducing the first dimension resolution.

Both configuration (B1) and (B2) had the same temperature programming since they are both capable of withstanding cryogenic temperatures. Configuration (B3) introduces a column which has a higher temperature limit than before, starting at 0 °C. Surprisingly, the still relatively

low temperature limit does not mean that the optimized oven programming starts at this temperature. Paraffins and olefins are not at all retained in the first dimension, making them elute quickly into the second column where, because of the low temperatures, these compounds are extremely well retained.

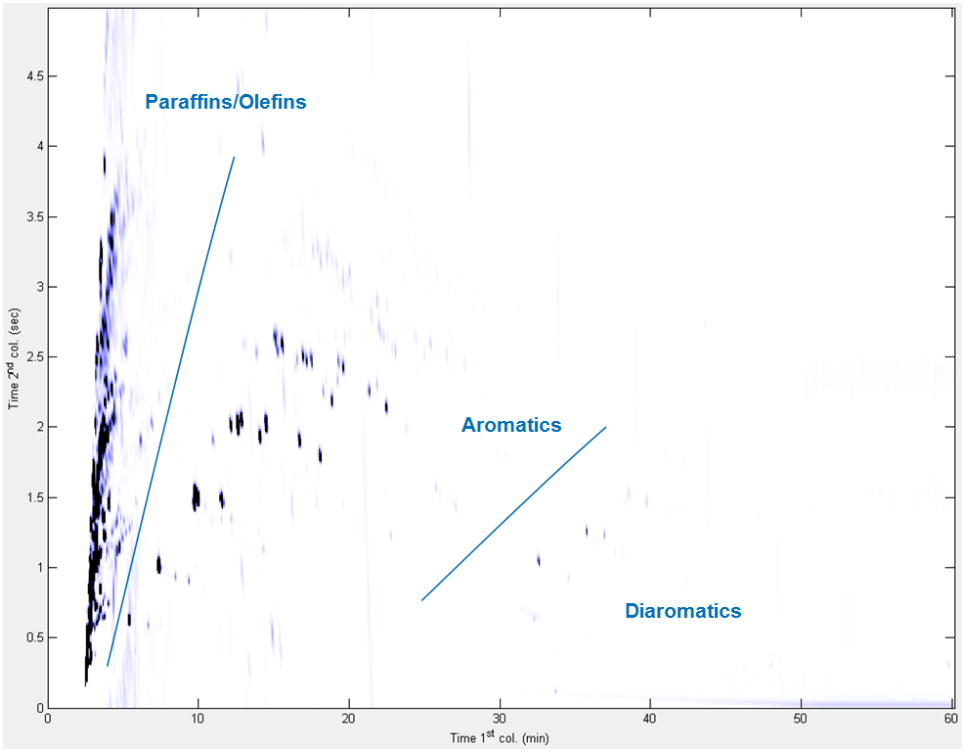


Figure 4.13 *– Optimized chromatogram obtained in configuration (B3)*

In fact, the separation achieved in Figure 4.13 had a starting temperature of 50 °C and rising by 3 °C/min until 200 °C, where it stayed for 10 minutes. This makes configuration (B3) a very quick analysis of merely one hour, nevertheless the fact that most compounds in the mixture are not well separated, eliminates this configuration from the list of viable ones.

Finally, since the DB-Wax phase proved to be good at least for the analysis of aromatics, configuration (B4) tries to take advantage of this fact in the reverse configuration, where there is no wrap-around by the diaromatics. The Wax phase has a lower temperature limit of 20 °C and this affects the separation quality, as can be seen in Figure 4.14. The optimized temperature program starts at 20 °C due to the column's minimum working temperature and maintains this temperature for 5 minutes, equivalent to the column's dead time. After these 5 minutes, the temperature increases for 2.5 °C/min until it reaches 220 °C, where it stays for 5 more minutes.

The paraffins and olefins share the same retention behavior as the one observed with configuration (B3), however, they are slightly more retained in the first dimension and the initial plateau in the oven programming causes a particular stacked "F" shape rather than the usual, more organized roof-tiling effect that is seen especially well in the aromatics section.

Again, the Wax phase shows, in reverse configuration, complementary results as it did in the normal configuration: an exceptional capability for separating aromatics by number of carbon atoms. Nevertheless, there is not an adequate separation in the paraffins/olefins section. To try as much as possible to avoid wrap-around, the modulation period is increased to 8 seconds but with high molecular weight paraffins and olefins being so highly retained in the second dimension, the wrap-around phenomenon is practically unavoidable. The intense bleeding at high temperatures is also a disadvantage from the use of the polyethyleneglycol phases, seeing as it can mask some of the diaromatic peaks, which are more retained in the first dimension.

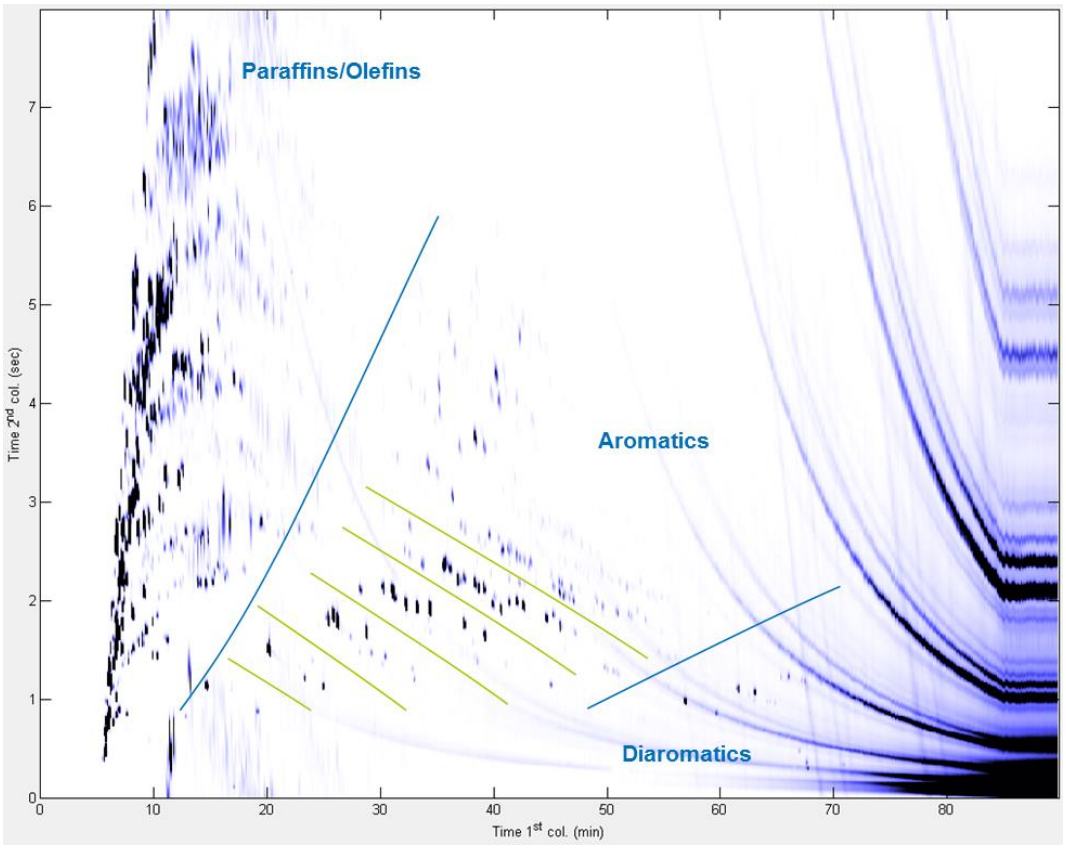


Figure 4.14 *– Optimized chromatogram obtained in configuration (B4)*

4.2 Microfluidic Setup

The microfluidic modulation system is more sensitive to some parameters than the cryogenic modulator. This means that small changes in analysis parameters will have larger effects than would be expected. Phase ratios (the ratio of the internal diameter of a column to the thickness of the stationary phase film) is more important, as is the modulation period, which makes conditions for the microfluidic modulator harder to optimize.

The different operating carrier gas flow rates in the two columns of the microfluidic modulator requires larger internal diameters for the second dimension rather than the first, as opposed to the cryogenic modulator. The second column should be wide enough to be capable of

withstanding the high flow rates necessary to completely and rapidly flush the accumulation capillary. This increase in flow rate also means that the second column must be longer than in the cryogenic modulation system, otherwise compounds would elute far too quickly to be properly separated.

4.2.1 Normal configuration

Starting with normal configuration, the first dimension is, as before, a dimethylpolysiloxane phase, albeit different from the one used in the cryogenic modulation experiments. It is, in essence the same stationary phase but with a different geometry to fit the needs of the modulation system. Configuration (C7) deviates slightly from this rule as it uses a (5%-phenyl)-methylpolysiloxane phase which gives it a minimal polarity, though it is still considered a non-polar column.

Table 4.7 *– Stationary phases used in the microfluidic normal configuration tests*

	1st dimension	2nd dimension	
	Manufacturer/product name length; internal diameter; film thickness Temperature limits	Manufacturer/product name length; internal diameter; film thickness Temperature limits	Active groups in stationary phase (Retention mechanism)
(C1)	Agilent J&W DB-1 20 m; 0.1 mm; 0.4 µm [-60 °C : 350 °C]	Agilent J&W DB-200 10 m ; 0.25 mm ; 0.25 µm [30 °C : 320 °C]	35% trifluoropropyl (Mid-polar)
(C2)	Agilent J&W DB-1 20 m; 0.1 mm; 0.4 µm [-60 °C : 350 °C]	Restek Rtx-200 7 m ; 0.2 mm ; 0.05 µm [-20 °C : 340 °C]	Trifluoropropyl (Mid-polar)
(C3)	Agilent J&W DB-1 20 m; 0.1 mm; 0.4 µm [-60 °C : 350 °C]	Restek Rtx-200 MS 10 m ; 0.25 mm ; 0.25 µm [-20 °C : 340 °C]	Trifluoropropyl (Mid-polar)
(C4)	Agilent J&W DB-1 10 m; 0.1 mm; 0.4 µm [-60 °C : 350 °C]	Restek Rtx-200 MS 10 m ; 0.25 mm ; 0.25 µm [-20 °C : 340 °C]	Trifluoropropyl (Mid-polar)
(C5)	Agilent J&W DB-1 20 m; 0.1 mm; 0.4 µm [-60 °C : 350 °C]	Restek Rtx-1701 10m ; 0.25 mm ; 0.5 µm [-20 °C ; 280 °C]	14% cyanopropylphenyl (Mid-polar)
(C6)	Agilent J&W DB-1 20 m; 0.1 mm; 0.4 µm [-60 °C : 350 °C]	Agilent J&W DB-1701 10 m ; 0.25 mm ; 0.25 µm [-20 °C ; 300 °C]	14% cyanopropylphenyl (Mid-polar)
(C7)	Agilent J&W DB-5 20 m; 0.1 mm; 0.4 µm [-60 °C : 350 °C]	Agilent J&W DB-1701 10 m ; 0.25 mm ; 0.25 µm [-20 °C ; 300 °C]	14% cyanopropylphenyl (Mid-polar)

For the second dimension, the stationary phases that performed best in the cryogenic normal configuration – the 14% cyanopropylphenyl phase and the trifluoropropyl phase – were selected to be tested with the microfluidic setup. As before, we have checked for columns available at IFPen that can withstand low temperatures in order to adequately separate the light compounds in gasolines. In the cryogenic setup, second dimensions had a constant phase ratio of 1:1000 (internal diameters of 0.1 mm and film thicknesses of 0.1 µm), however, unique to the microfluidic modulator, a columns with different phase ratios were tested, to observe the effect this has on separation quality. In Table 4.7 the list of column combinations used in the microfluidic modulation system in normal configuration is presented. As stated, the configurations used in the microfluidic setup reflect the best results from the cryogenic setup. In the second dimension, configurations (C1) through (C4) use trifluoropropyl phases while (C5) through (C7) use cyanopropylphenyl phases. Configuration (C1) has a distinct disadvantage over all the others since the minimum working temperature of the DB-200 column is 30 °C. The appropriate flow rate for the first dimension was calculated with HP Flow Calc 2.0, as was the length of the bleeding capillary, as explained in chapter **Erro! A origem da referência não foi encontrada.**. For the second dimension, a flow rate that is typically used with the microfluidic modulator to adequately flush the accumulation capillary was used. The fill/flush times were calculated with the equations present in Appendix 1. Of note is the fact that FID 1 (the detector at the end of the second column) does not require make-up gas due to the high flow rates used in the second dimension. The operating conditions used are detailed in Table 4.8.

Table 4.8 *– Optimized operating conditions using configuration (C1)*

Injection	Split/Splitless Inlet; 300 °C; 1:500 Split Ratio; 0.1 µl
Carrier Gas	Helium; 0.25 ml/min (1st dimension); 20 ml/min (2nd dimension)
Oven Program	30 °C (0.5 min) → 2 °C/min → 250 °C (0 min)
Modulation	5 s (4.85 s fill time; 0.15 s flush time)
FID 1	300 °C; 100 Hz; H_2 - 40 ml/min; Air – 400 ml/min; He (make-up) - 0 ml/min
FID 2	300 °C; 100 Hz; H_2 - 40 ml/min; Air – 400 ml/min; He (make-up) - 25 ml/min
Bleed Capillary	Fused Silica; length – 1.29 m; internal diameter – 0.05 mm

The results obtained are presented in Figure 4.15 and illustrate the problem with using a column that does not function at low temperatures. Not only does the high temperature cause compounds to not be very well separated in the first dimension but it also prevents adequate retention in the second dimension. Perhaps the existence of a secondary oven could have improved the separation quality but unfortunately the chromatograph used in the microfluidic experiments does not have the necessary attachment.

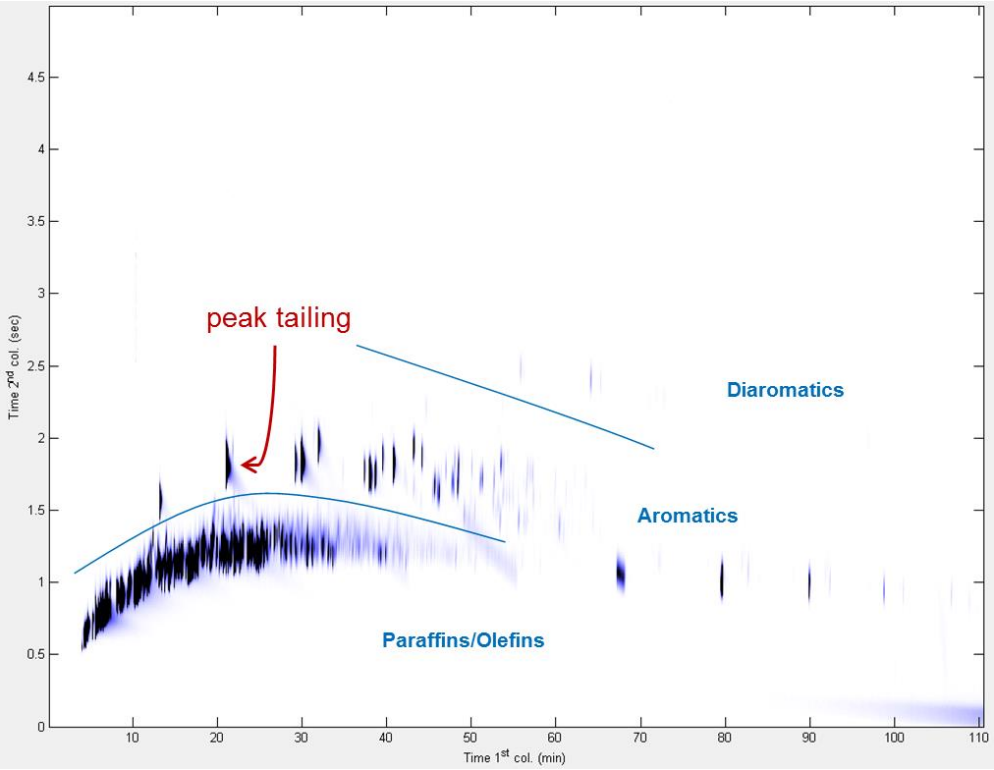


Figure 4.15 *– Optimized chromatogram obtained in configuration (C1)*

There is also some first dimension peak tailing. Previous tests conducted with the very same modulator used in these experiments also display this tailing problem (Boiron, Souchon 2015) and the definitive cause is not yet known for certain. The most likely explanation involves the fact that the columns are connected to the modulator, which basically consists of two flow redirection units – essentially flow splitters. The connection might not be perfect which may cause the formation of dead volumes within the splitters, thus inducing band broadening inside the modulator. Regardless, this tailing is more or less evident in all the ensuing results.

Configuration (C2) employs a very unique column in the second dimension. Not only does it have a shorter length and smaller internal diameter than the others, it has an extremely thin film. This column can also withstand temperatures down to -20 °C which would help with the separation. The temperature programming was, therefore, changed to a starting temperature of -20 °C and increasing 2 °C/min until reaching the maximum temperature of 250 °C. Unfortunately, the particular geometry of the second column forced some less wanted changes. The fact that its internal diameter was so small meant that the flow rate of the second dimension had to be decreased from 20 ml/min to 10 ml/min to avoid reaching pressures at the inlet that are above the ones can be handled by the pressure controller. This was still not enough to avoid the inlet from reaching the pressure at which it safely shuts down, so the maximum program temperature was also reduced to 220 °C in a further attempt to decrease the maximum pressure in the inlet. Figure 4.16 shows the result of this analysis.

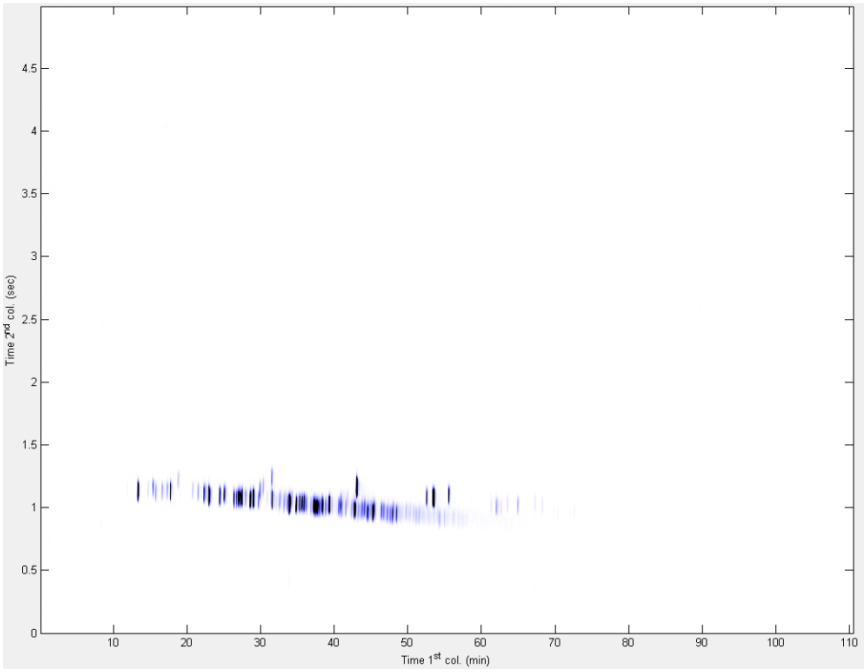


Figure 4.16 *– Chromatogram obtained in configuration (C2)*

All the constraints imposed on the analysis conditions were not enough to make the separation work as intended. For such a sensitive setup as the microfluidic system, all these changes provoked an increase in retention in the first dimension and consequently a decrease in retention in the second one, further hindered by the very thin film, so much so that there is not even a clear separation between families.

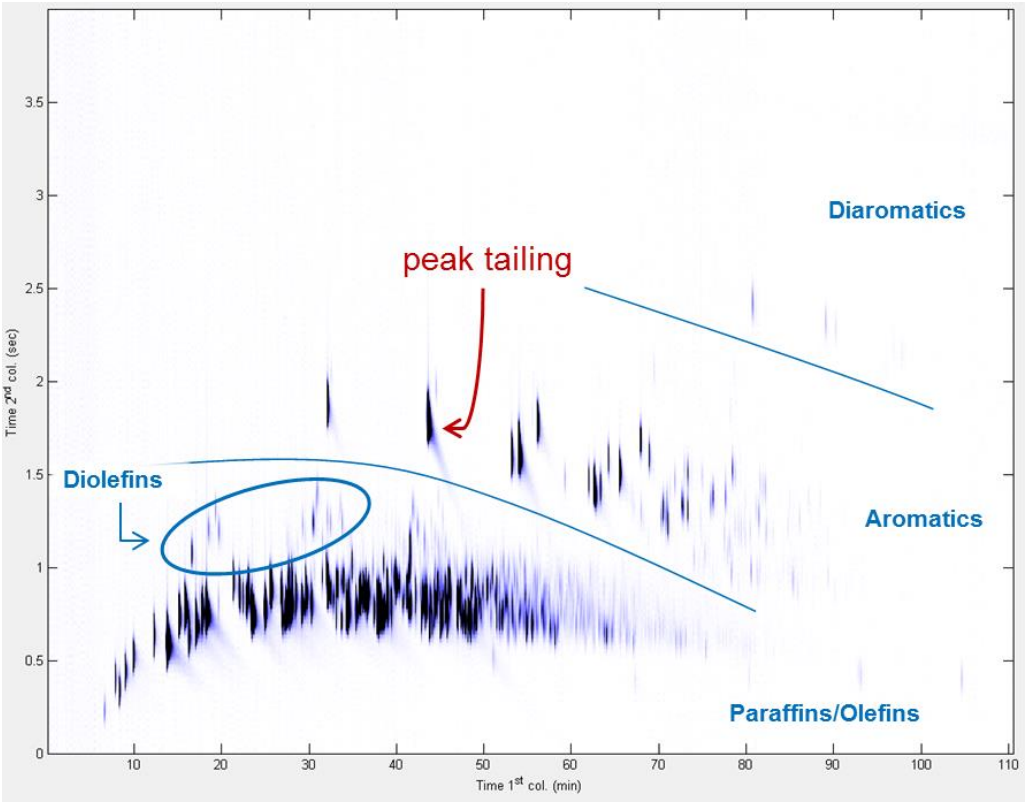


Figure 4.17 *– Optimized chromatogram obtained in configuration (C3)*

Considering the previous separation, a second column with a more typical phase ratio was used in configuration (C3). The 2D flow rate was returned to its usual value of 20 ml/min and the maximum temperature of the program was reverted to 250 °C. The modulation period was also shortened from 5 to 4 seconds, and the flush time was corrected accordingly. The chromatogram in Figure 4.17 looks extremely similar to the chromatogram obtained from configuration (A3) which is be expected since the same stationary phases were used. The best separation so far, configuration (C3) provides some separation of diolefins from the main paraffins and olefins section, as well as a decent roof-tiling effect of the aromatics. The peak tailing in the first dimension is, however still an issue since it increases the potential for co-elutions mainly within the paraffins/olefins section. Furthermore, the retention behavior observed in configuration (A3) is identical to this one with the column losing selectivity at higher temperatures.

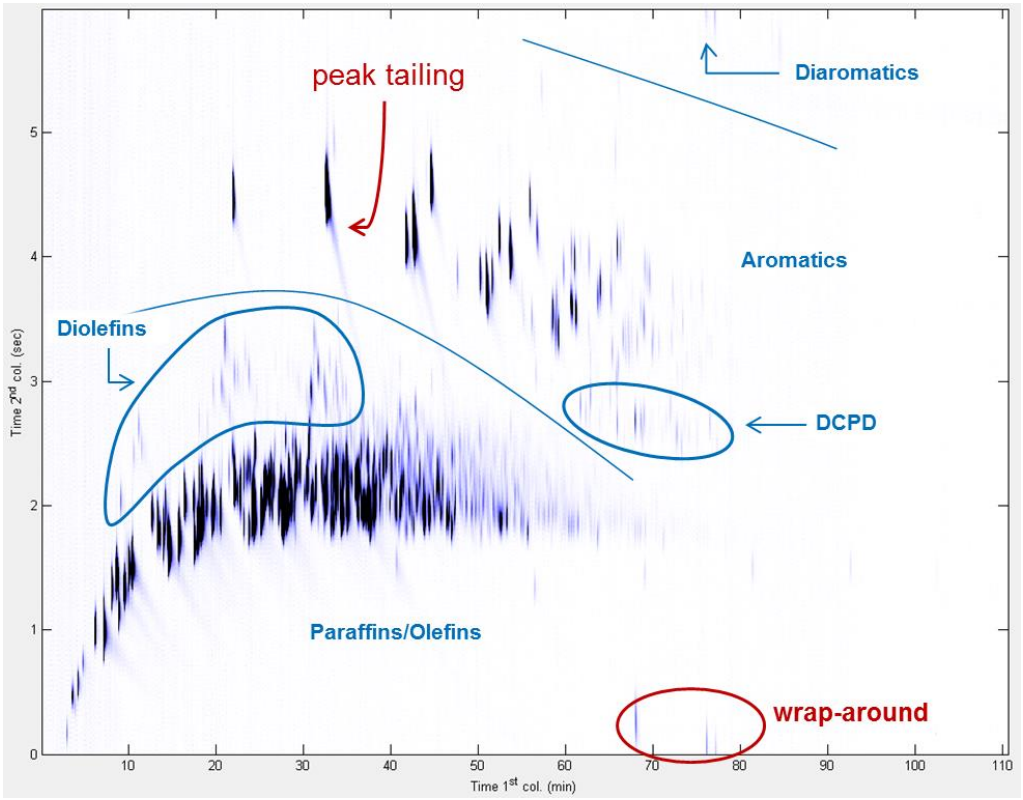


Figure 4.18 *– Optimized chromatogram obtained in configuration (C4)*

Since all the compounds elute within approximately 2.5 seconds from each other in the second dimension, configuration (C4) considers a shorter first dimension of just 10 meters. This should allow compounds to be more retained in the second dimension since they arrive at lower temperatures. Figure 4.18 shows exactly this phenomenon.

Configuration (C4) sacrifices some first dimension resolution by using a shorter column and a longer modulation period. However, this improves the second dimension separation, especially in the diolefins section, and the DCPD area of the chromatogram. The ever-present peak tailing

continues to unavoidably influence the analysis in a negative way, as is the wrap-around of the diaromatics. The existence of wrap-around even with the characteristic decline of selectivity from the Rtx-200 phase means that the first dimension was cut slightly shorter than it should have been, which led to the increase in retention of the diaromatics. This, however is not as critical, as no co-elutions are observed.

With the pretty satisfactory separation achieved using configuration (C4), the next column combinations rely on the 14% cyanopropylphenyl phases in the second dimension rather than the trifluoropropyl phases. Configuration (C5) begins this portion of the tests with a relatively high stationary phase film thickness for the column in the second dimension, though the operating parameters from the previous analysis are maintained except for the modulation period, which is shortened from 6 to 5 seconds. Figure 4.19 shows the chromatogram resulting from the analysis using configuration (C5).

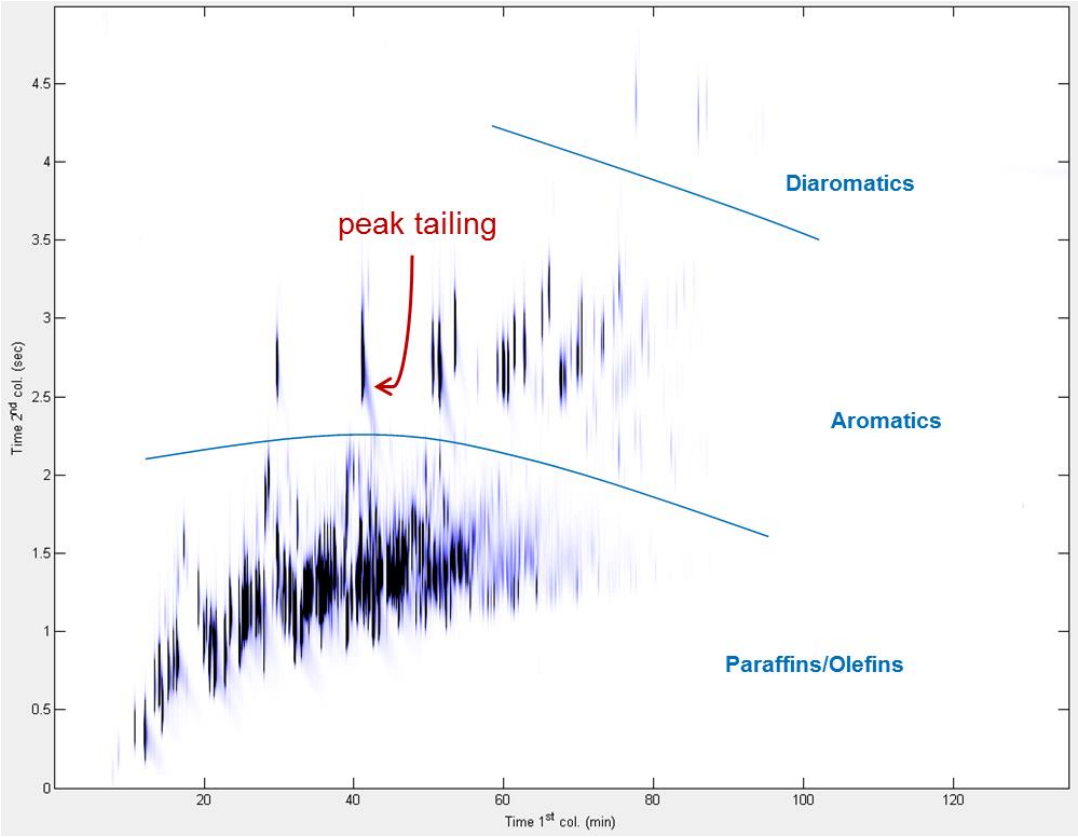


Figure 4.19 *– Optimized chromatogram obtained in configuration (C5)*

The peaks observed in this analysis are slightly more structured than the ones that have been appearing with the trifluoropropyl phases, since the selectivity of the stationary phase does not decrease with high temperatures. This is evidenced by the presence of a pronounced roof-tiling effect in the aromatics section of the chromatogram. In spite of this, the line between diolefins and the remaining paraffins and olefins is somewhat ambiguous since the peaks are quite wide

in the second dimension. The first dimension tailing also persists throughout the analysis in the more concentrated peaks like toluene.

Its flaws aside, the analysis performed with configuration (C5) is a decent analysis even if not up to par with configuration (C4). Configuration (C6) aims at using a different phase ratio to further enhance the analysis quality. The results shown in Figure 4.20 are a clear improvement over all previous analyses.

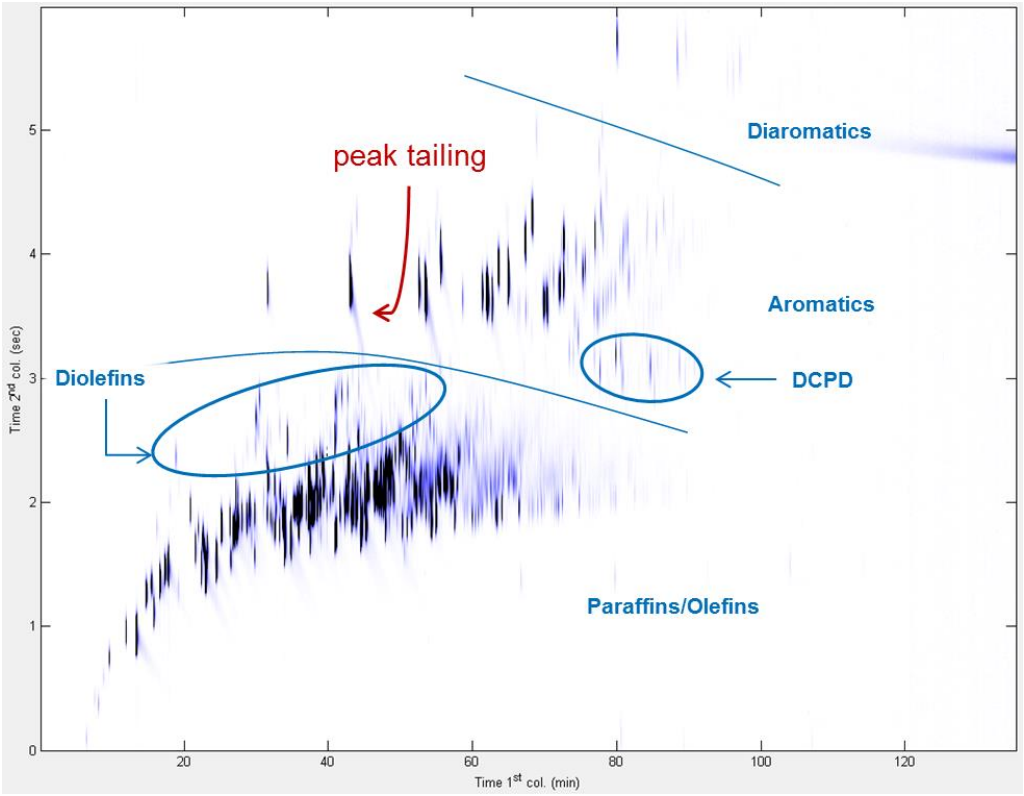


Figure 4.20 *– Optimized chromatogram obtained in configuration (C6)*

Diolefins are more clearly separated from the remaining compounds in the bottom of the chromatogram and the DCPD compounds are also in a distinct zone from the aromatics. The thin peaks in the second dimension caused by the decrease in stationary phase film thickness help improve the overall resolution of the chromatogram. The increase of modulation period from 5 to 6 seconds completely avoids the wrap-around problem unlike what happened with configuration (C4). The decrease in second dimension film thickness also helps to make the first dimension tailing seem less prominent, thus making the chromatogram seem cleaner than the ones obtained from configurations (C4) and (C5).

Lastly, configuration (C7) was a last-ditch effort to diminish tailing as much as possible, effectively changing the first dimension stationary phase to a different, still non-polar, phase. These optimized parameters for this configuration keep the exact same operating conditions as configuration (C6) in order to clearly distinguish differences between the results obtained using the DB-1 and DB-5 stationary phases. Figure 4.21 shows the result of this final test.

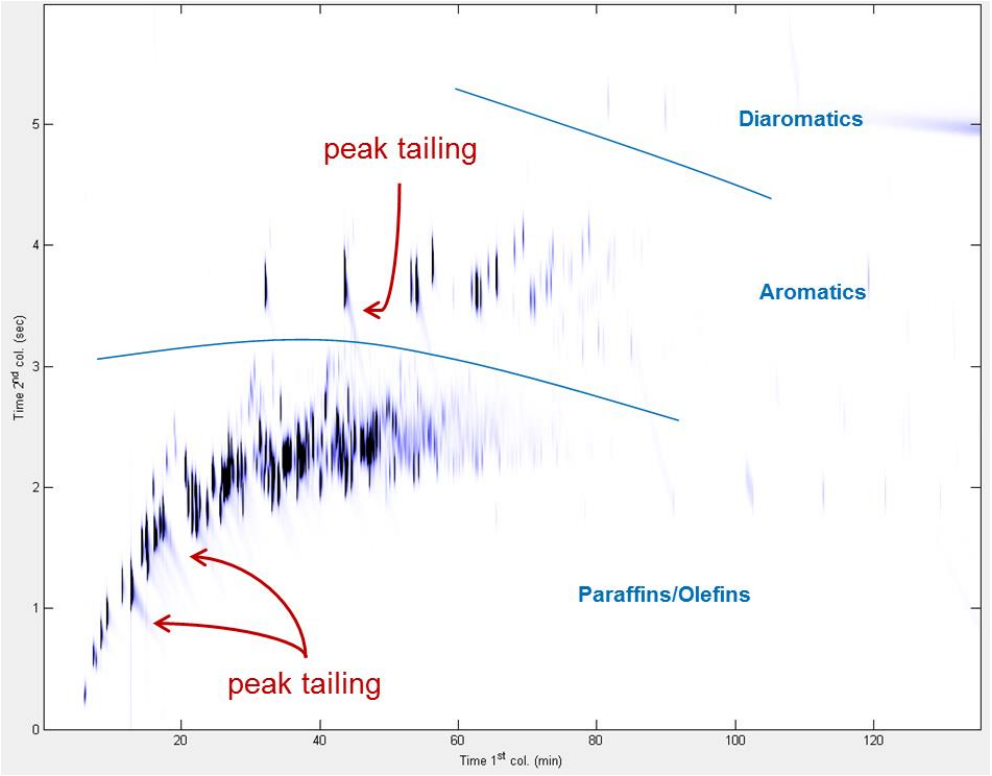


Figure 4.21 *– Optimized chromatogram obtained in configuration (C7)*

Tailing in the more concentrated peaks (e.g. Toluene) still exists in the results, although less noticeable. Regrettably, there is an appearance of first dimension tailing in peaks where tailing has not been very prevalent since configuration (C3), which is in the zone of the light paraffins. This, coupled with the fact that compounds in the paraffins and olefins region of the chromatogram don't seem to be as well separated as they were in configuration (C6), renders configuration (C7) ultimately obsolete and indicates that peak tailing is not due to the type of stationary phase used in the first dimension.

4.2.2 Reverse configuration

The microfluidic modulator's restriction on column geometries make selection of stationary phases a bit more problematic. Polydimethylsiloxane columns are so useful and versatile that there are a lot of variations in geometry and phase ratio. Unfortunately, manufacturers don't have such a diversity when it comes to polar columns. However, at this point in the project, the best stationary phase has been consistently a 14% cyanopropylphenyl phase, therefore, the column selection for the reverse configuration has been narrowed down to one column combination. Table 4.9 specifies the column combination chosen. The second dimension is a non-polar dimethylpolysiloxane column which was chosen based on its availability and phase ratio. The column length was set as 10 meters in order to keep the dimensions from previous analysis. This means that the bleeding capillary must be changed, since the pressure drop in a 0.32 mm column is much smaller the previous ones with 0.25 mm.

Table 4.9 *– Stationary phase used in the microfluidic reverse configuration tests*

	1st dimension		2nd dimension
	Manufacturer/product name length; internal diameter; film thickness Temperature limits	Active groups in stationary phase (Retention mechanism)	Manufacturer/product name length; internal diameter; film thickness Temperature limits
(D1)	Restek Rtx-1701 20 m; 0.1 mm; 0.1 µm [-20 °C : 280 °C]	14% cyanopropylphenyl (Mid-polar)	Agilent J&W DB-1 10 m ; 0.32 mm ; 0.1 µm [-60 °C : 350 °C]

Table 4.10 provides the information regarding the optimized operating conditions for this column configuration and Figure 4.22 shows the resulting chromatogram.

Table 4.10 *– Optimized operating conditions using configuration (D1)*

Injection	Split/Splitless Inlet; 300 °C; 1:500 Split Ratio; 0.1 µl
Carrier Gas	Helium; 0.20 ml/min (1st dimension); 20 ml/min (2nd dimension)
Oven Program	-20 °C (0.5 min) → 2 °C/min → 250 °C (0 min)
Modulation	6 s (5.9 s fill time; 0.1 s flush time)
FID 1	300 °C; 100 Hz; H_2 - 40 ml/min; Air – 400 ml/min; He (make-up) - 0 ml/min
FID 2	300 °C; 100 Hz; H_2 - 40 ml/min; Air – 400 ml/min; He (make-up) - 5 ml/min
Bleed Capillary	Fused Silica; length – 9.5 m; internal diameter – 0.1 mm

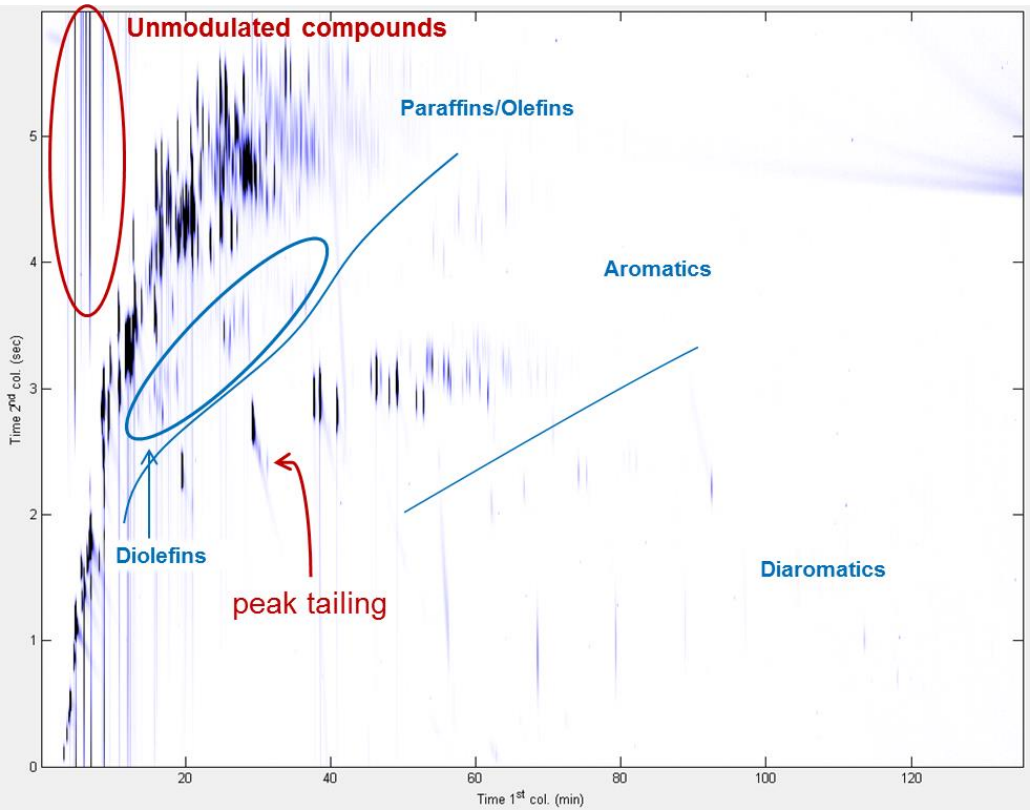


Figure 4.22 *– Optimized chromatogram obtained in configuration (D1)*

As expected, the separation quality is akin to configuration (B1). Diolefins are adequately separated as are DCPD's. The separation in the main paraffins and olefins area is not as interesting as the cryogenic setup configuration since the second dimension peak widths are quite large. A bit more retention in the first dimension would have improved the analysis since, not only would it help reduce the modulation period, it would also increase resolution in the paraffins area. That said, the separation is quite good and is suitable for gasoline analysis. One problem in these results unrelated to optimization is a phenomenon that causes the peak some of the less retained and more concentrated compounds to show some fronting. There was unfortunately not enough time to fix this problem before the report's due date.

4.3 Modulator Comparison

Overall, both modulators produced satisfactory results, despite their different operation principles. In a direct comparison, the same analysis has greater resolution in the cryogenic setup because of its ability to produce much thinner peaks than the microfluidic modulator. This flaw is all the more important considering the high propensity for peak tailing in the microfluidic setup. A great advantage in running an analysis in a valve-based system is the fact that there is no need for cryogenic fluid, making the analysis much cheaper and eliminating some possible malfunctions such as freezing tubes or jets. Regardless, the cryogenic system is much easier to optimize and more versatile than the microfluidic. An important benefit of the cryogenic system is that, since it uses relatively small second dimension flow rates, it can be connected to a mass spectrometer, making it ideal for research purposes. The microfluidic system is more suited to routine analysis due to its comparatively low run cost. A summary of the advantages and disadvantages of each system is organized in Table 4.11.

Table 4.11 *– Comparison of the different types of modulation*

Cryogenic Modulation		**Microfluidic Modulation**	
Pros:	**Cons:**	**Pros:**	**Cons:**
• Extremely high resolution; • Simple operation; • Easy method optimization; • Robust; • MS Friendly.	• Higher initial investment (cryogenic infrastructure); • Use of expensive cryogenic fluid; • High maintenance.	• Easy assembly and operation; • Cheaper investment and use; • Adequate resolution.	• Tailing problems in the first dimension; • Sensitive to small changes in phase ratio and flush time (hard optimization); • Not possible to connect MS.
Verdict: The higher resolution means that the cryogenic modulation is more suitable for research purposes and is a great tool for method development due to the ease of parameter optimization.		**Verdict:** Considering the slight loss in resolution versus the steep reduction in both investment and running costs, the microfluidic system seems fit for routine analyses of well-known mixtures.	

5 Applications

Using some of the more successful column combinations and experimental conditions, experiments were performed in order to demonstrate the power, usefulness and practicality of the optimized analyses.

5.1 Analysis of Different Gasoline Types

Samples originating from diverse refining processes have similar but still noticeably different compositions. Therefore, to test the versatility of the optimized setups, analyses were made on the different samples listed in Table 5.1. The tests utilized the best configurations from both modulation systems and the chromatograms available in Appendix II using the FID as the detector.

Table 5.1 *– Gasolines analyzed using the various different setups*

Sample name	Gasoline Type
S8244 (1500626-001)	FCC effluent
ASTM D5134 Reference	Reformate
U016-3023-4 (1404119-001)	HDT effluent
S9147 (1500483-001)	Pygas
S8997 (1500954-001)	FCC effluent
Cut 15-150 (1405531-001)	Oligomerization

Particularly in cryogenic setup, tests were also run using the mass spectrometer, detecting ions in a range of molecular mass from 10 to 300 at a frequency of 50 Hz. These results need to be further examined in order to identify and quantify the species present in each sample. To date, because it represents an intensive work, only the FCC effluent S8244 GC×GC-MS data could be exploited in detail as depicted in the section 5.2.

5.2 Detailed Hydrocarbon Analysis

As stated in section 5.1, MS analyses were made for every one of the different gasoline samples. The FCC effluent sample S8244 (the one used to optimize the method parameters) was chosen to be subjected to detailed hydrocarbon analysis. The objective of this procedure is to identify as many of the compounds present in the sample as possible. In traditional methods, there is a database with the retention indices of each compound (basically the retention time of each individual compound relative to the nearest linear paraffins), however, no such database exists for GC×GC analysis of gasolines. Using the identification capabilities of the MS, this task is made possible. The MS analysis was done in configuration (A2) and the results are shown in **Erro! A origem da referência não foi encontrada.** using the GC Image software.

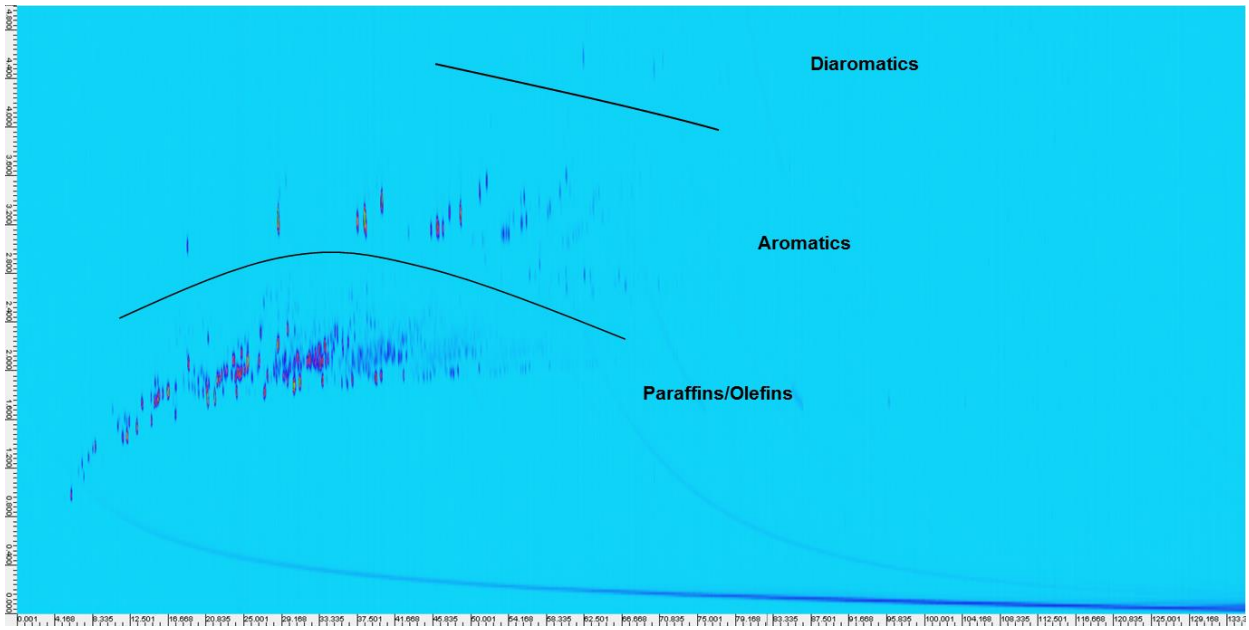


Figure 5.1 *– Mass spectrometry res*ults for the FCC effluent *S8244 (Total Ion Current)*

In order to assure a good identification of compounds, the GC×GC results were cross-checked with the IFP0104 standard method results for the very same sample. Using this method, a lot of the compounds identified in the standard method were also easily identified in the bidimensional chromatogram. Appendix III has a list of the compounds for which the standard method provided structural identification, as well as an indication of which compounds were also found in the GC×GC method. Figure 5.2 illustrates the compounds that were found with the cross-checking technique.

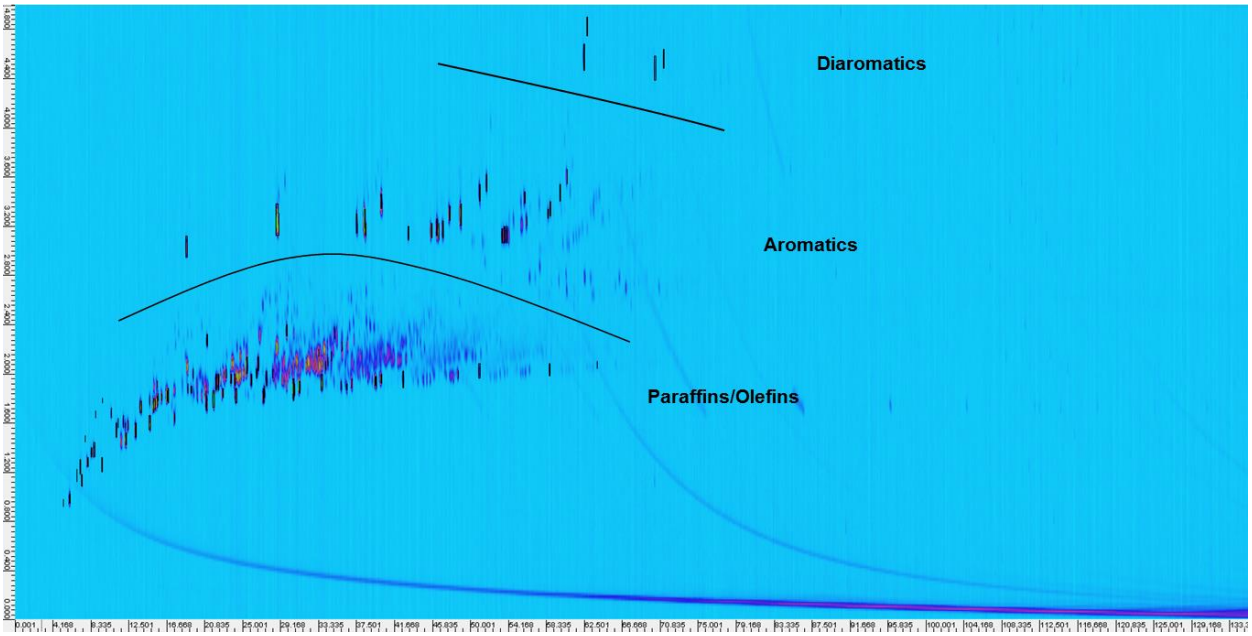


Figure 5.2 *– Cross-checked chromatogram (compounds verified found in black)*

Still, clearly there are a lot more compounds that can be observed in the chromatogram but aren't structurally identified in the standard 1D GC method results. This happens because a lot

of co-elutions happen in the traditional GC method but are avoided by the second separation in GC×GC, thus revealing more compounds that would be otherwise obscured by very intense peaks like the lighter aromatics (benzene, toluene and xylenes).

Focusing on small sections on the chromatogram it is possible to grasp the power of the GC×GC-MS setup. In the diaromatics section, the standard method identified three naphthalene species, along with benzothiophene. Even with GC×GC, it is difficult to see any other compounds in that region of the chromatogram, however, there is an option in the software that allows the user to see the chromatogram of specific ions. The selected ion chromatograms are an extremely useful tool to find specific compounds.

Figure 5.3 shows how, by selecting ions that corresponds to the molecular weight of the compounds, GC×GC-MS becomes even more sensitive and allows the identification of additional compounds under the condition the molecular ion is detected.. Thus, besides the naphthalene, benzothiophen and methylnaphthalenes (all present in the standard method results) can be easily identified with GC×GC-MS.

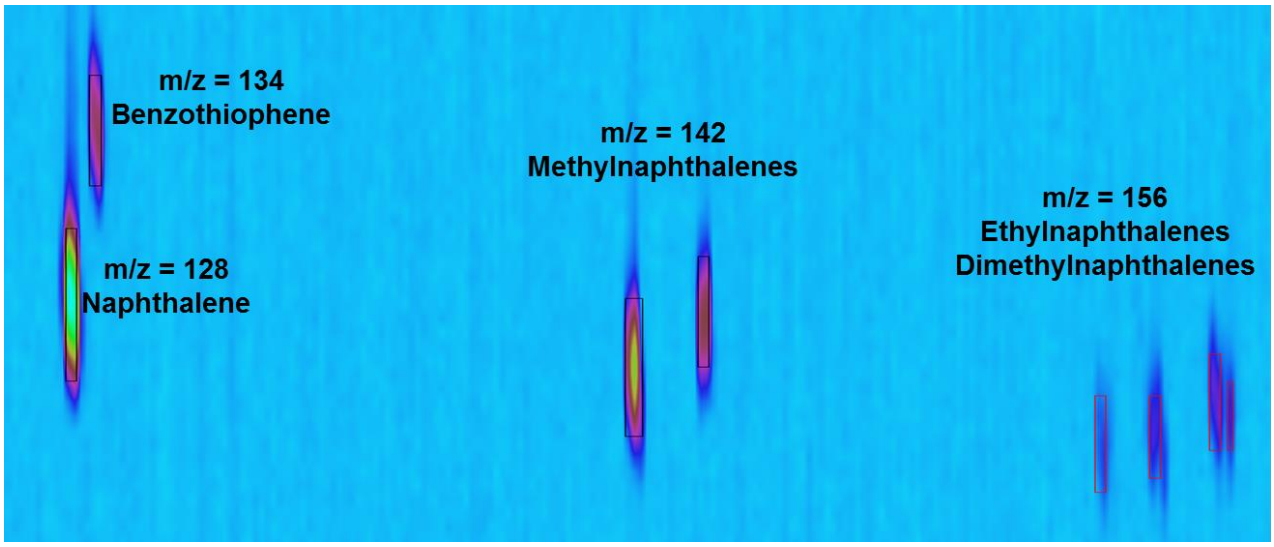


Figure 5.3 *– Diaromatics section of the chromatogram with selected ion signal*

Similarly, in the aromatics section, benzene, toluene, ethylbenzene and the xylenes are easily identifiable, however a closer look at the chromatograms reveals that a lot more compounds are present, as evidenced by Figure 5.4. Besides the typical aromatics, several thiophenic compounds are identified, as is styrene, a typically difficult compound to find in a traditional analysis.

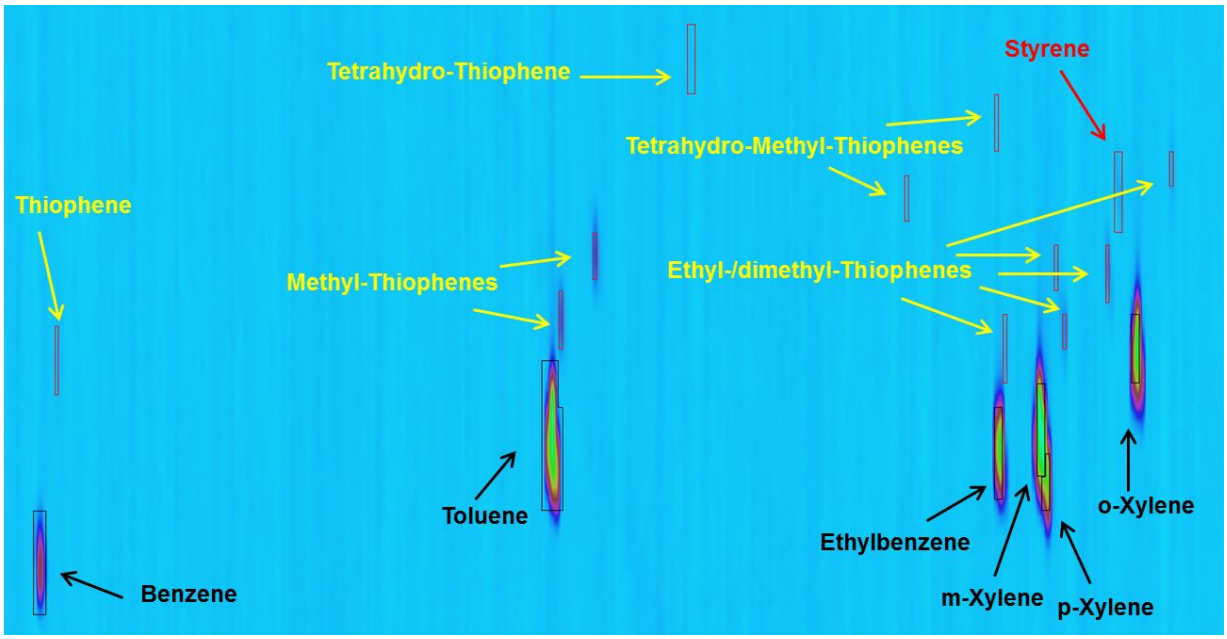


Figure 5.4 *– Aromatics region of the chromatogram*

These are only some examples of the compounds that are able to be found using GC×GC-MS but many more compounds that were not present in the compound list were identified such as phenols, indenics and diolefins.

5.3 Other analyses

Section 5.1 focused on some of the analyzed gasoline samples. This, however, is not a comprehensive list of all the analyzed samples.

Samples of upgraded bio oil were requested to be analyzed in the cryogenic setup in both the normal and reverse configuration. The same was accomplished with effluents from the fast catalytic pyrolysis of biomass.

A synthetically prepared solution attempting to emulate bio pyrolysis oil was also injected using the best cryogenic/reverse configuration (B1) in order to better characterize the reactions that take place during the processes used in the production of these kinds of fuels.

These results are not shown in the manuscript as they are only isolated analyses that were outside of the scope of this project which was focused on GC×GC analysis of gasolines with both cryogenic and microfluidic modulators.

Appendix IV presents the silicon speciation experiments in detail. These served to demonstrate the great sensitivity of the GC×GC by injecting solutions with very low concentrations of silicon compounds.

6 Conclusions

Optimal conditions were achieved for the analysis of gasoline samples in both cryogenic and microfluidic modulation techniques in normal and reverse configurations. The best stationary phase combinations for each setup and column configuration involved the use of a non-polar, dimethylpolysiloxane column as well as a 14% cyanopropylphenyl serving as the best polar phase. In fact, mid-polarity phases such aforementioned cyanopropylphenyl phase and the trifluoropropyl phase were the best at general-purpose separation, providing the most comprehensively good quality along the whole analysis between the different families and within the different sections of the chromatogram. Highly polar phases such as the polyethyleneglycol phase are more suited the separation of aromatics rather than paraffins or olefins, thus having a niche use. Ideally, stationary phases with lower minimum programmable temperatures were found to be optimal for the analysis of gasoline samples since the lower temperatures facilitate the adequate separation of light compounds.

Regarding the performances of each modulation system, the cryogenic modulator yielded results with extremely high resolution, thus lending itself to use in research oriented projects while the affordability and ease of use of the microfluidic modulator are better suited for routine or on-line analysis.

Detailed hydrocarbon analysis of complex gasoline mixtures shows particular promise due to GC×GC chromatograms being remarkably structured. Chromatogram structure facilitates family and carbon number identification and, coupled with mass spectrometry results, this could lead to the creation of standard methods.

Looking for perspectives, due to lack of time, there was only one column selection used to test the reverse configuration in the microfluidic modulation system. It would be worthwhile to test more stationary phases and geometries in this setup, even if they are end up not being as good as the one tested.

Further exploration of the MS results obtained from the analysis in the cryogenic system for the different samples would also be an endeavor worth pursuing with the ultimate goal to try and create a standard method for the analysis of gasolines with GC×GC.

Derivations of compounds gasoline samples such the use maleic anhydride to eliminate conjugated diolefins from a given sample and bromine to achieve the same with olefins could help to very easily identify these compounds in GC×GC. For example, in configurations with a good separation of diolefins from the main group of paraffins and olefins, it would be easy to realize which peaks disappear when comparing a raw sample with a sample made to react with maleic anhydride.

References

Adahchour, M.; Beens, J.; Vreuls, R. J. J.; Batenburg, A. M.; Brinkman, U. A. Th. (2004): Comprehensive two-dimensional gas chromatography of complex samples by using a 'reversed-type' column combination: application to food analysis. In *Journal of Chromatography A* 1054 (1-2), pp. 47–55.

Adam, Frédérick; Thiébaut, Didier; Bertoncini, Fabrice; Courtiade, Marion; Hennion, Marie-Claire (2010): Supercritical fluid chromatography hyphenated with twin comprehensive two-dimensional gas chromatography for ultimate analysis of middle distillates. In *Journal of chromatography. A* 1217 (8), pp. 1386–1394.

Beens, J.; Adahchour, M.; Vreuls, R. J.J.; van Altena, K.; Udo A. T. B. (2001): Simple, non-moving modulation interface for comprehensive two-dimensional gas chromatography. In *Journal of Chromatography A* 919 (1), pp. 127–132.

Bertoncini, F.; Courtiade-Tholance, M.; Thiébaut, D.; Jones, T. (2013): Gas chromatography and 2D-gas chromatography for petroleum industry. The race for selectivity: Editions Technip.

Boiron, M.; Souchon, V. (2015): Evaluation of a differential flow modulator for bidimensional gas chromatography (GC×GC).

Dallüge, J.; Beens, J.; Brinkman, U. A. Th. (2003): Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool. In *Journal of Chromatography A* 1000 (1-2), pp. 69–108.

Duhamel, C.; Cardinael, P.; Peulon-Agasse, V.; Firor, R.; Pascaud, L.t; Semard-Jousset, G. et al. (2015): Comparison of cryogenic and differential flow (forward and reverse fill/flush) modulators and applications to the analysis of heavy petroleum cuts by high-temperature comprehensive gas chromatography. In *Journal of chromatography. A* 1387, pp. 95–103.

Dutriez, Thomas; Courtiade, Marion; Thiébaut, Didier; Dulot, Hugues; Bertoncini, Fabrice; Hennion, Marie-Claire (2010): Extended characterization of a vacuum gas oil by offline LC-high-temperature comprehensive two-dimensional gas chromatography. In *Journal of separation science* 33 (12), pp. 1787–1796.

Elder, Jr., J. F.; Gordon, B. M.; Uhrig, M. S. (1986): Complex Mixture Analysis by Capillary-to-Capillary Column Heartcutting GC/MS. In *Journal of Chromatographic Science* 24.

Finley, M. (2012): The Oil Market to 2030--Implications for Investment and Policy. In *EEEP* 1 (1).

Griffith, J. F.; Winniford, W. L.; Sun, K.; Edam, R.; Luong, J. C. (2012): A reversed-flow differential flow modulator for comprehensive two-dimensional gas chromatography. In *Journal of Chromatography A* 1226, pp. 116–123.

Guiochon, G.; Gonnord, M. F.; Zakaria, M.; Beaver, L. A.; Siouffi, A. M. (1983): Chromatography with a Two-Dimensional Column. In *Chromatographia* 17 (3).

Javed, A. (2012): The Hydrogenation of Pyrolysis Gasoline (PyGas) Over Nickel and Palladium Catalysts. School of Chemistry University of Glasgow.

Nizio, K. D.; McGinitie, T. M.; Harynuk, J. J. (2012): Comprehensive multidimensional separations for the analysis of petroleum. In *Journal of Chromatography A* 1255, pp. 12–23.

Omais, B.; Courtiade, M.; Charon, N.; Esnault, S.; Thiébaut, D. (2012): Reversal of elution order in a single second dimension by changing the first column nature in comprehensive two-dimensional gas chromatography. In *Journal of Chromatography A* 1255, pp. 196–201. DOI: 10.1016/j.chroma.2012.07.042.

Ong, R.; Marriott, P.; Morrison, P.; Haglund, P. (2002): Influence of chromatographic conditions on separation in comprehensive gas chromatography. In *Journal of Chromatography A* 962 (1-2), pp. 135–152.

Phillips, J. B.; Xu, J. (1995): Comprehensive multi-dimensional gas chromatography. In *Journal of Chromatography A* 703 (1-2), pp. 327–334.

Poole, S. K.; Poole, C. F. (2008): The orthogonal character of stationary phases for gas chromatography. In *Journal of separation science* 31 (6-7), pp. 1118–1123.

Schoenmakers, P.; Marriott, P.; Beens, J. (2003): Nomenclature and Conventions in Comprehensive Multidimensional Chromatography. In *LC-GC Europe*.

Seeley, J. V.; Micyus, N. J.; Bandurski, S. V.; Seeley, S. K.; McCurry, J. D. (2007): Microfluidic deans switch for comprehensive two-dimensional gas chromatography. In *Analytical Chemistry* 79 (5), pp. 1840–1847.

Semard, G.; Gouin, C.; Bourdet, J.; Bord, N.; Livadaris, V. (2011): Comparative study of differential flow and cryogenic modulators comprehensive two-dimensional gas chromatography systems for the detailed analysis of light cycle oil. In *Journal of chromatography. A* 1218 (21), pp. 3146–3152.

Speight, J. G. (2006): The Chemistry and Technology of Petroleum. 4th: CRC Press.

Toulhoat, H.; Raybaud, P. (2013): Catalysis by transition metal sulphides. From molecular theory to industrial application: Editions Technip (IFP Énergies nouvelles, publications).

Vendeuvre, C.; Ruiz-Guerrero, R.; Bertoncini, F.; Duval, L.; Thiébaut, D. (2007): Comprehensive Two-Dimensional Gas Chromatography for Detailed Characterisation of Petroleum Products. In *Oil & Gas Science and Technology - Rev. IFP* 62 (1), pp. 43–55.

Appendix I – Microfluidic Modulator Fill/Flush Calculations

As stated in chapter 3, it is important that no compounds are detected in FID 2. To ensure that this doesn't happen, one must first make sure that the bleeding capillary dimensions are such that the flow rate in the bleeding capillary is the same than the flow rate in the first dimension. This is performed using a column pressure/flow calculator to calculate the appropriate bleeding capillary length to go to FID 2.

Adjusting the ratio of the volume that gets into the capillary during the fill cycle and the volume that gets flushed out in the flush cycle is another important step in avoiding loss of sample through FID 2. It has been shown (Boiron, Souchon 2015) that the amount of volume flushed should be at least 1.5 times the volume filled for a 0.53 ID capillary tubing. Inequation A1 relates the two concepts:

$$\frac{Q_{2D} * t_i}{Q_{1D} * (t_m - t_i)} \geq 1.5 \quad \text{(I1)}$$

In which Q_{1D} and Q_{2D} are the first and second dimension flow rates respectively, t_m is the total modulation period and t_i is the flush (or injection – into the second column) time. Having a ratio bigger than 1.5 is not a problem, however doing so would sacrifice resolution since it means that not only is the focusing effect on the compounds lessened, the modulation period could possibly be shortened as well, which would increase first dimension resolution.

The last, more obvious restriction is that the accumulation capillary should not be overfilled. This means that the fill volume should not be superior to the volume of the accumulation capillary. Thus follows Inequation A2:

$$\frac{14.7}{P_{mod} + 14.7} * Q_{1D} * (t_m - t_i) < \pi * ID^2 * l \quad \text{(I2)}$$

In which ID is the internal diameter of the accumulation capillary and l is its length, and P_{mod} is the pressure at the modulator in psi. The first term in A2 corrects for the real volume of the gas inside the modulation loop with regards to the pressure.

Appendix II – Chromatograms of different gasoline samples

In section 5.1 the analysis of several types of gasoline is evoked. In this appendix, the resulting chromatograms are presented by sample with the different setups.

II.1 – S8244 (1500626-001) – FCC effluent

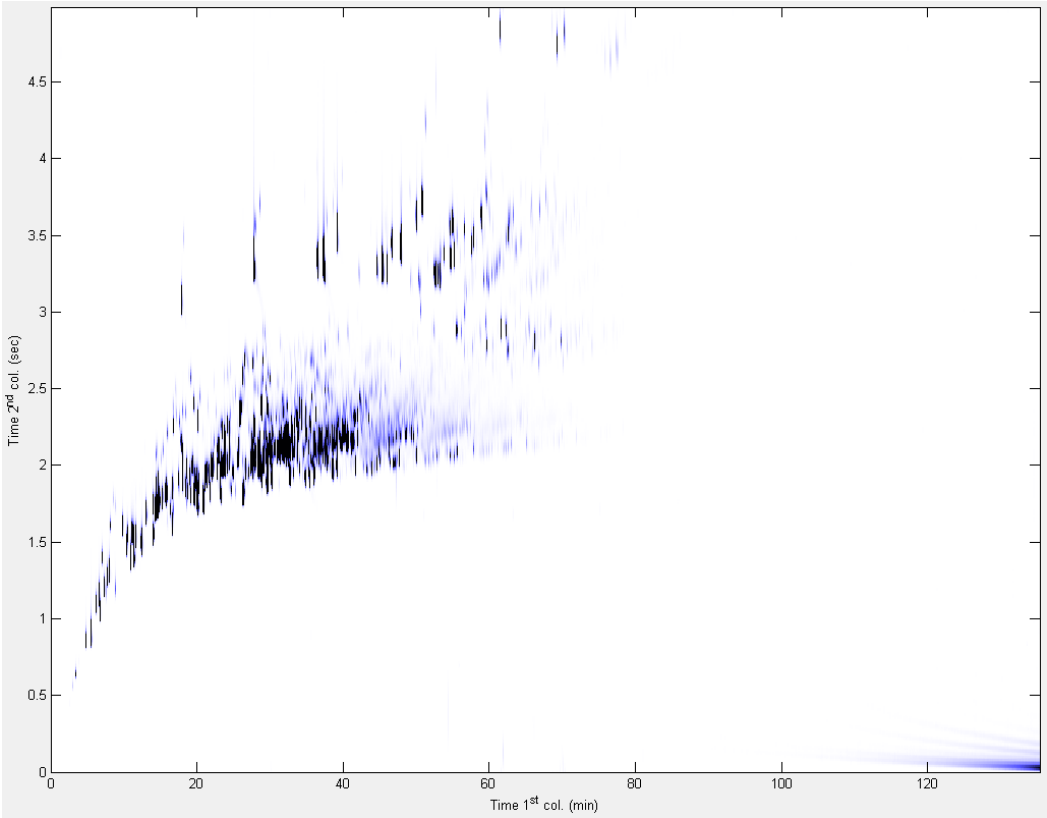


Figure II.1 *– Sample: S8244; Modulator: Cryogenic; Configuration: Normal (A2)*

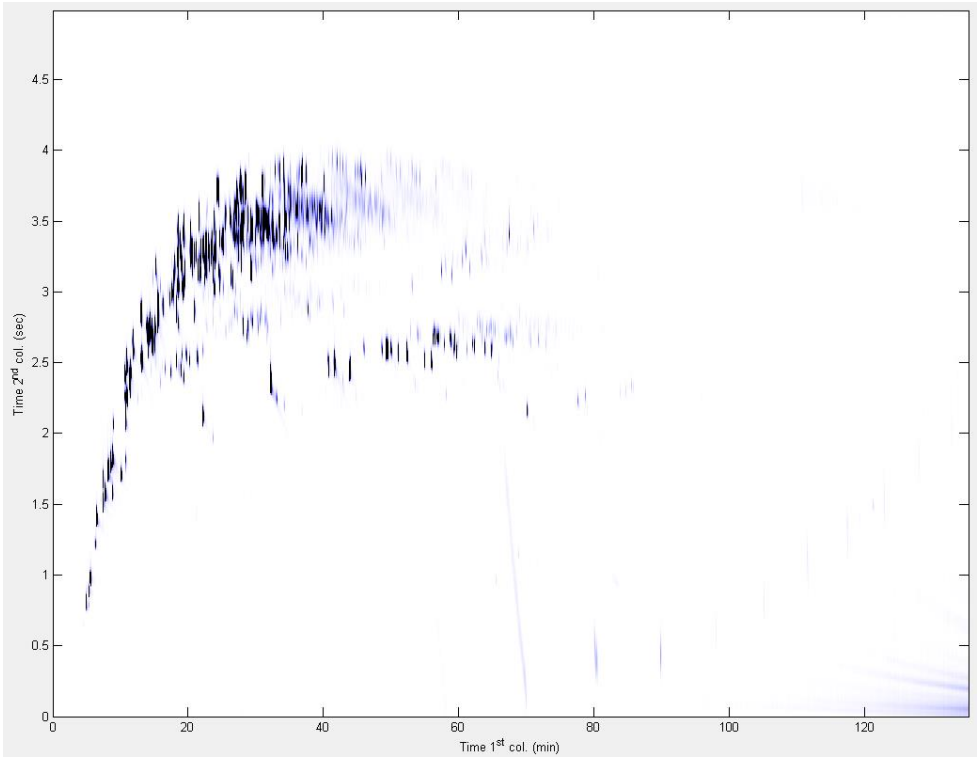


Figure II.2 *– Sample: S8244; Modulator: Cryogenic; Configuration: Reverse (B1)*

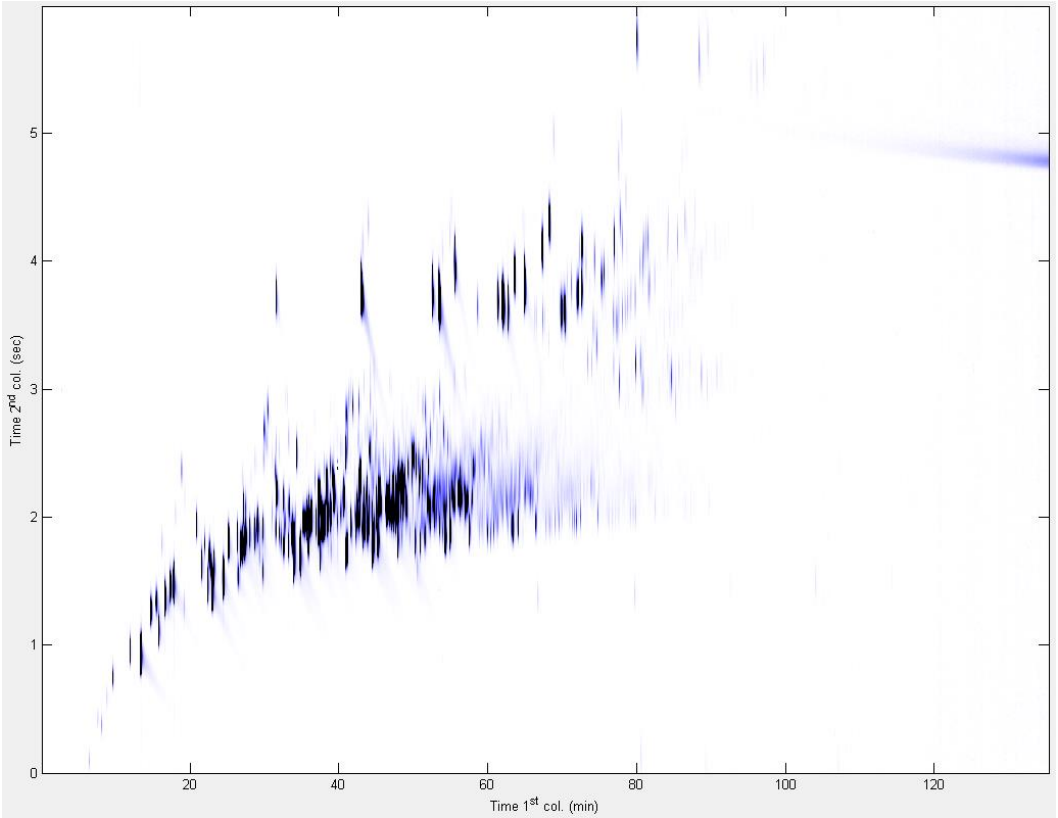


Figure II.3 *– Sample: S8244; Modulator: Microfluidic; Configuration: Normal (C6)*

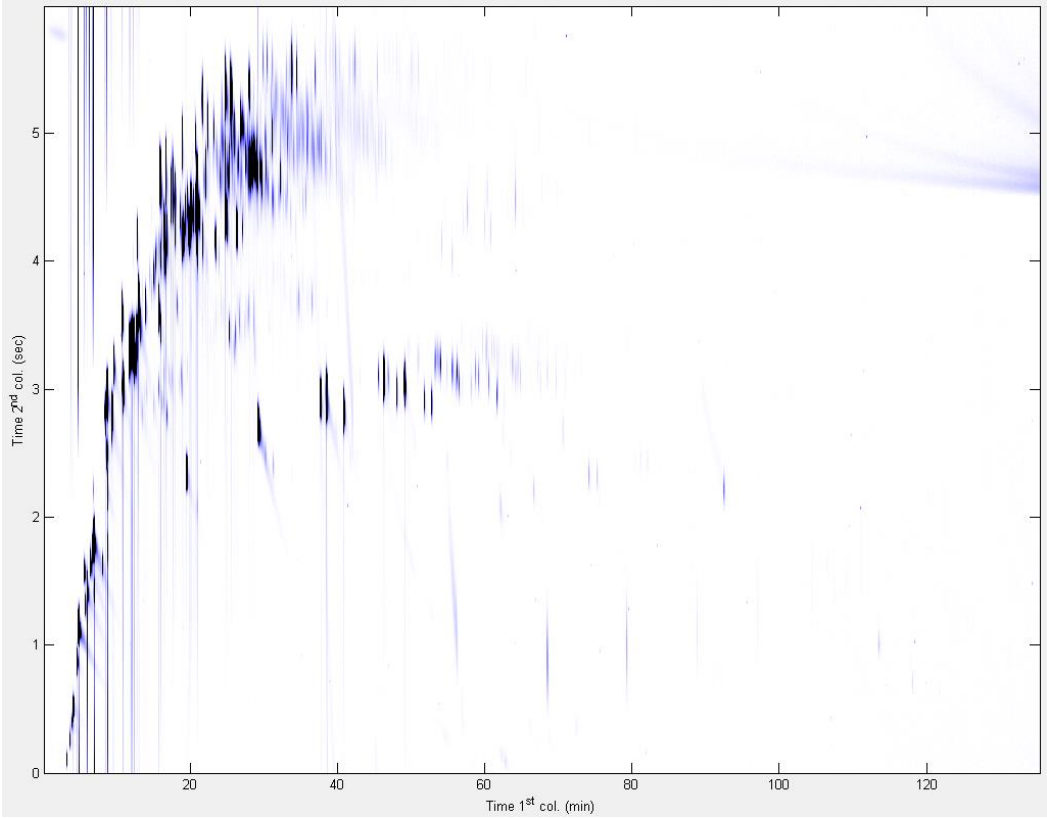


Figure II.4 *– Sample: S8244; Modulator: Microfluidic; Configuration: Reverse (D1)*

II.2 - ASTM D5134 Reference (Reformate)

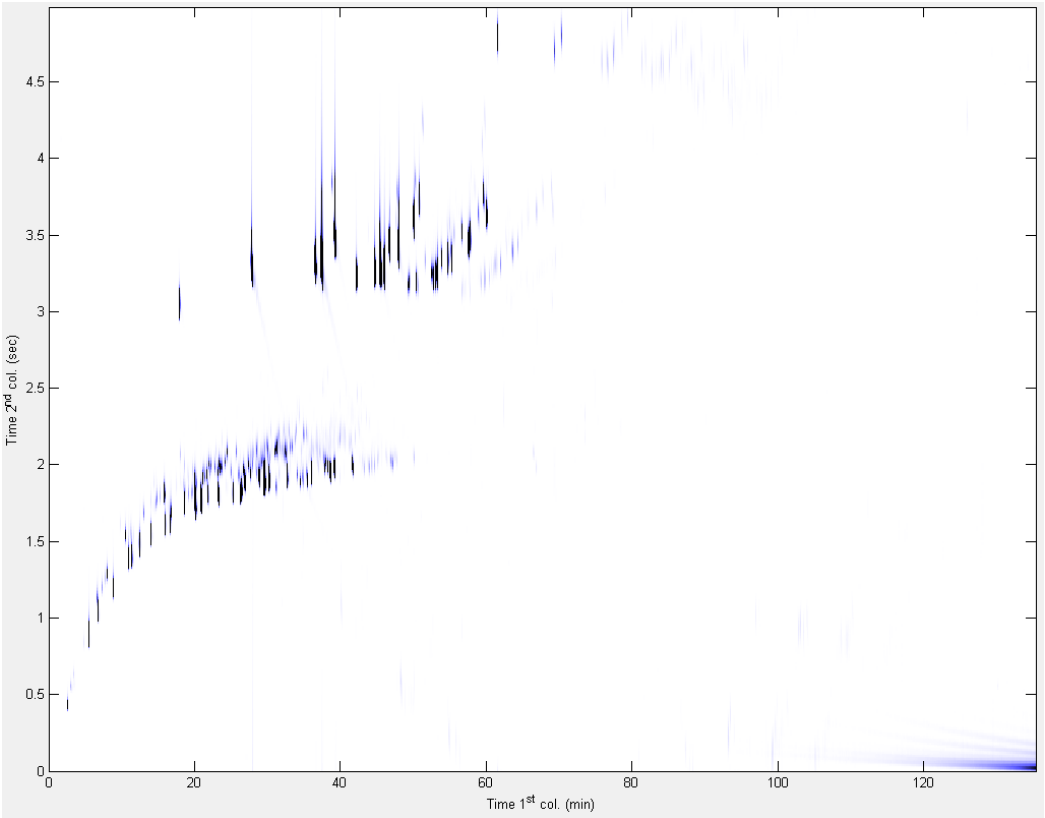


Figure II.5 *– Sample: Reformate; Modulator: Cryogenic; Configuration: Normal (A2)*

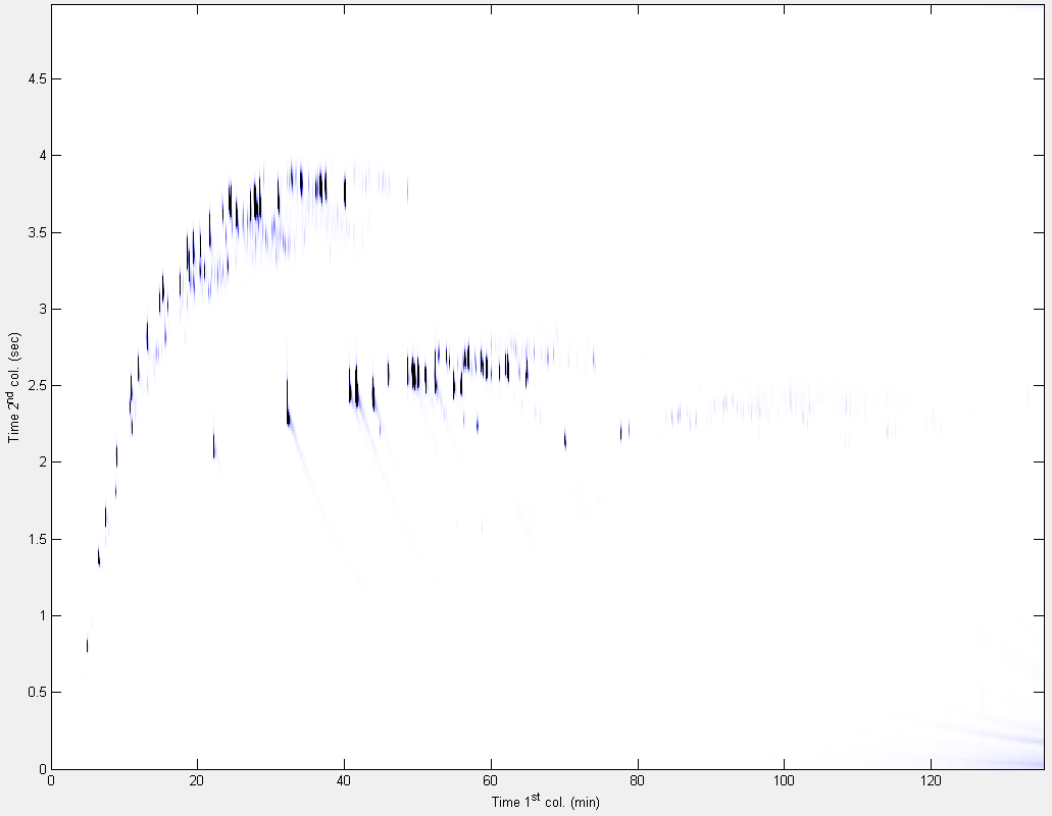


Figure II.6 *– Sample: Reformate; Modulator: Cryogenic; Configuration: Reverse (B1)*

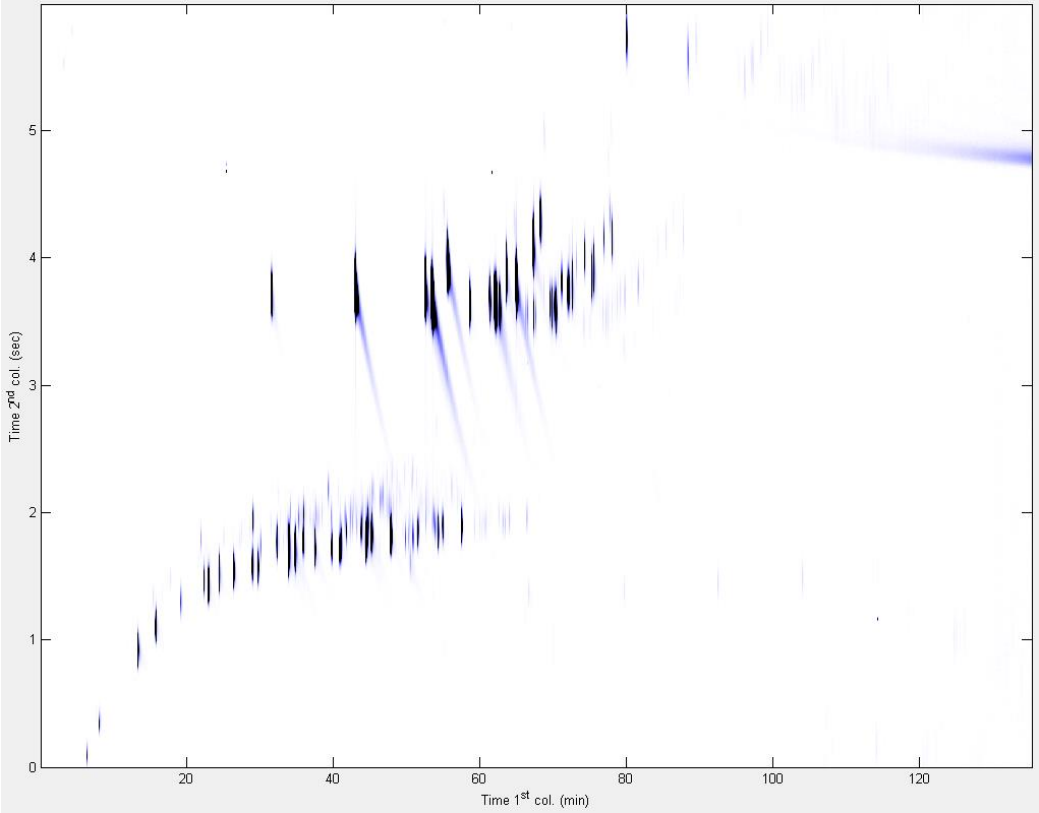


Figure II.7 *– Sample: Reformate; Modulator: Microfluidic; Configuration: Normal (C6)*

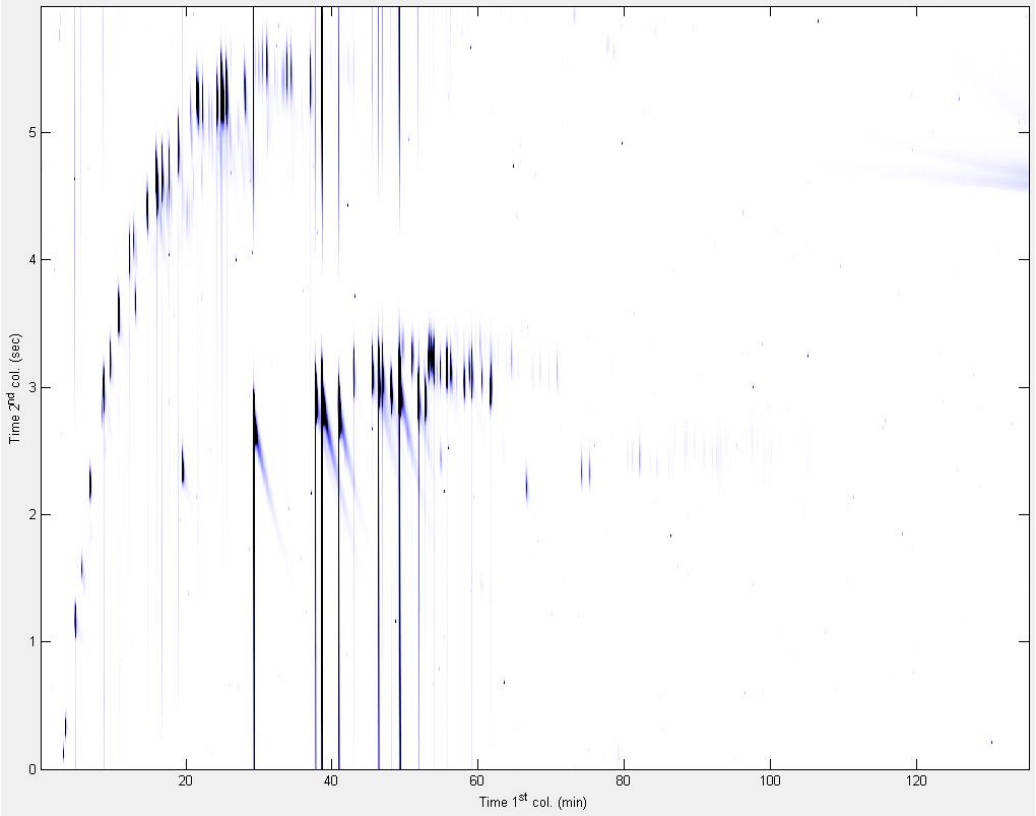


Figure II.8 *– Sample: Reformate; Modulator: Microfluidic; Configuration: Reverse (D1)*

II.3 - U016-3023-4 (1404119-001) - HDT effluent

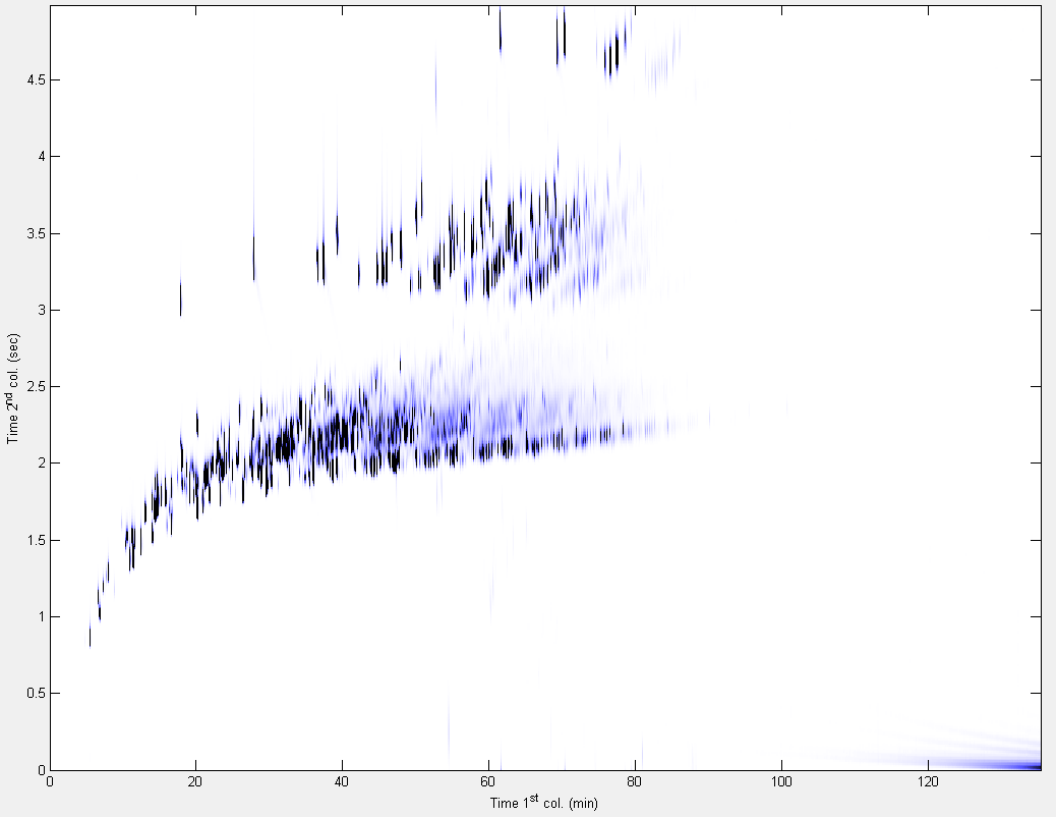


Figure II.9 *– Sample: HDT effluent; Modulator: Cryogenic; Configuration: Normal (A2)*

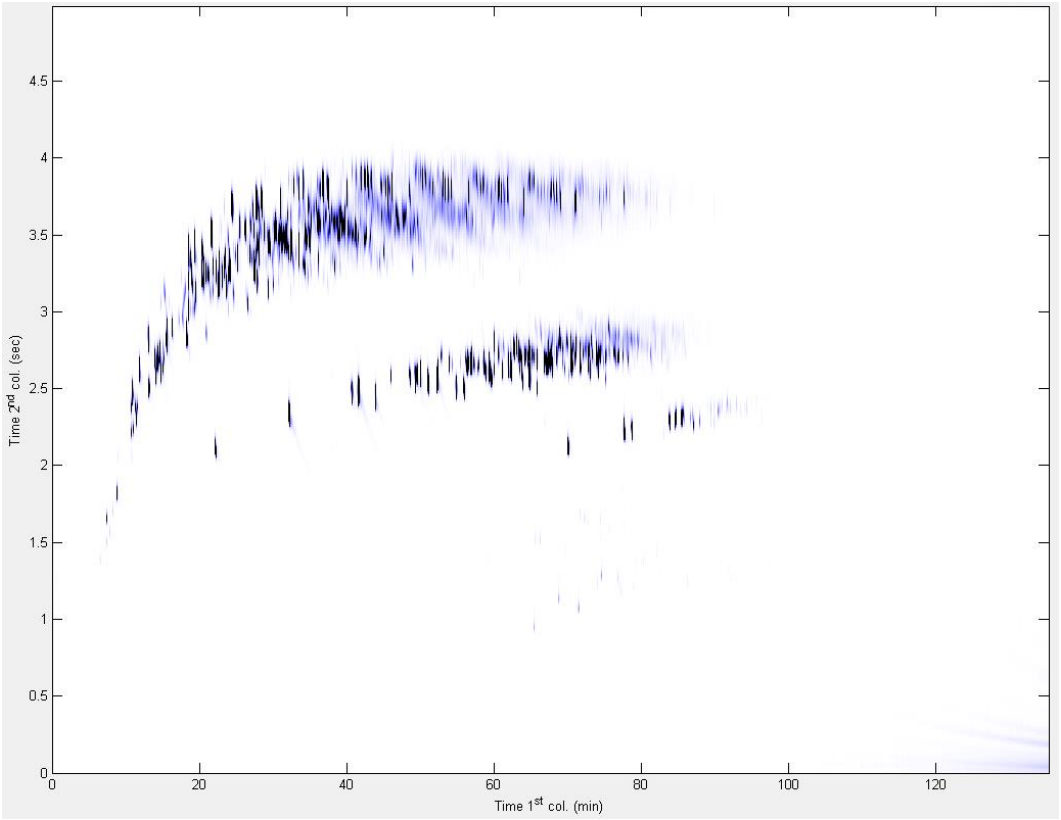


Figure II.10 *– Sample: HDT effluent; Modulator: Cryogenic; Configuration: Reverse (B1)*

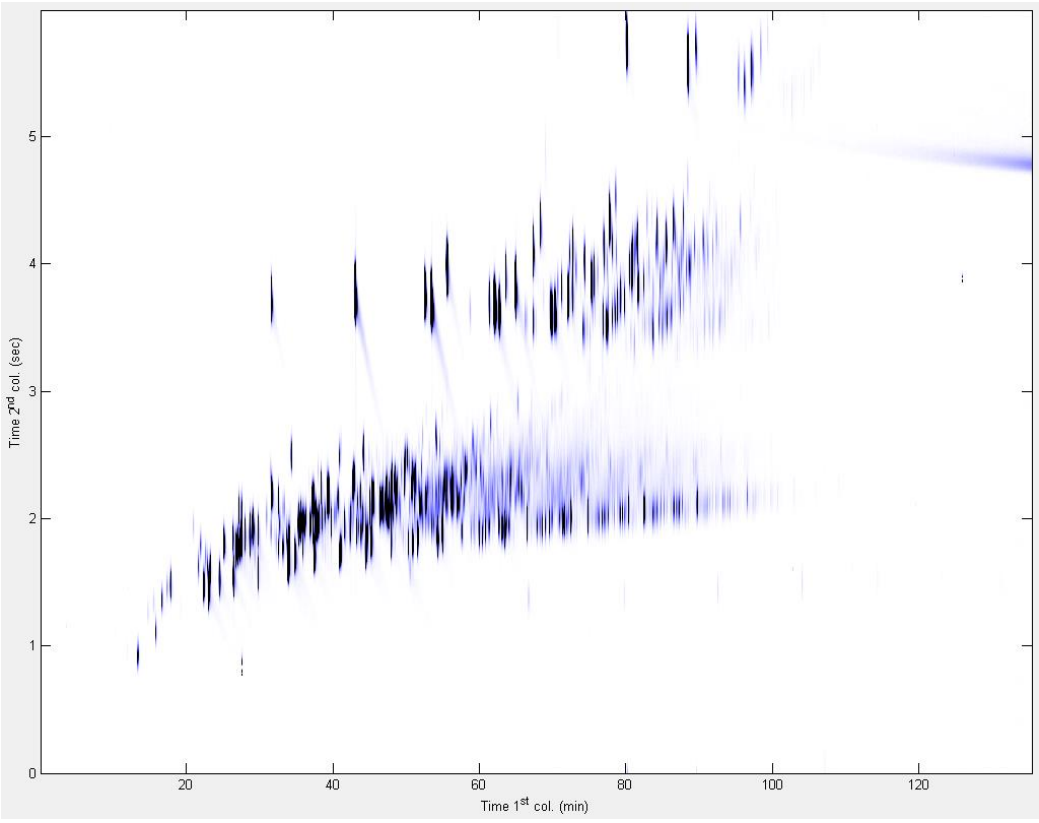


Figure II.11 *– Sample: HDT effluent; Modulator: Microfluidic; Configuration: Normal (C6)*

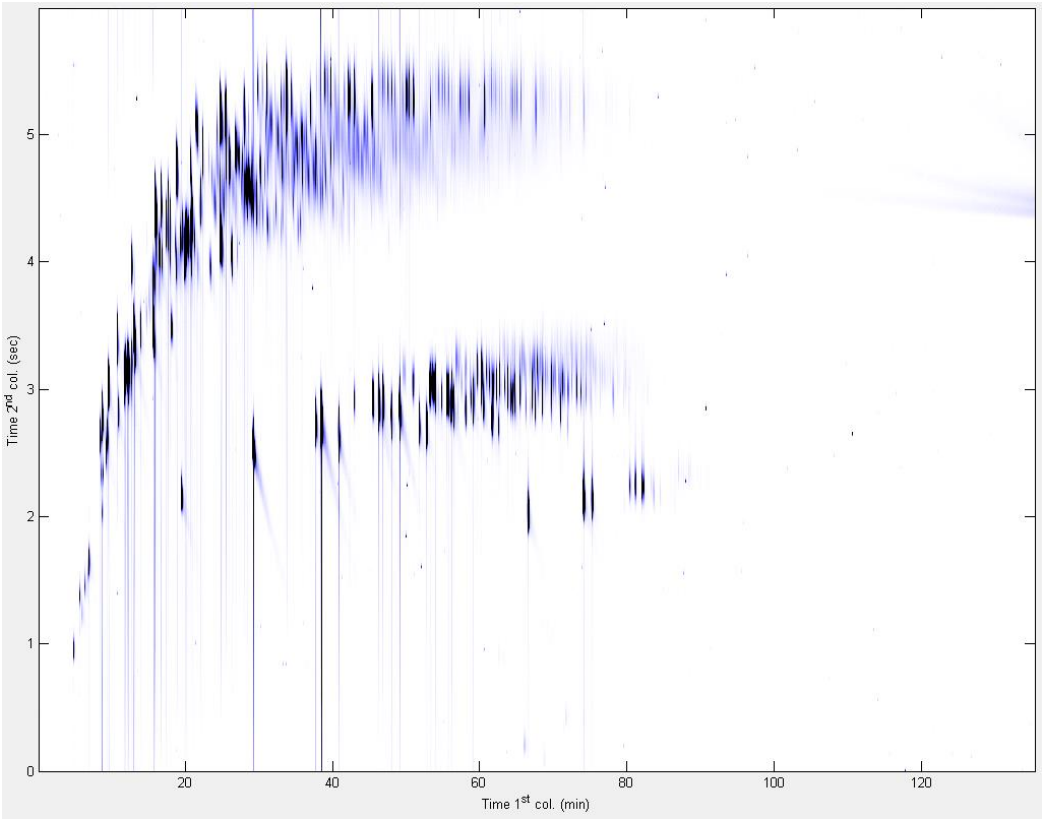


Figure II.12 *– Sample: HDT effluent; Modulator: Microfluidic; Configuration: Reverse (D1)*

II.4 - S9147 (1500483-001) - Pygas

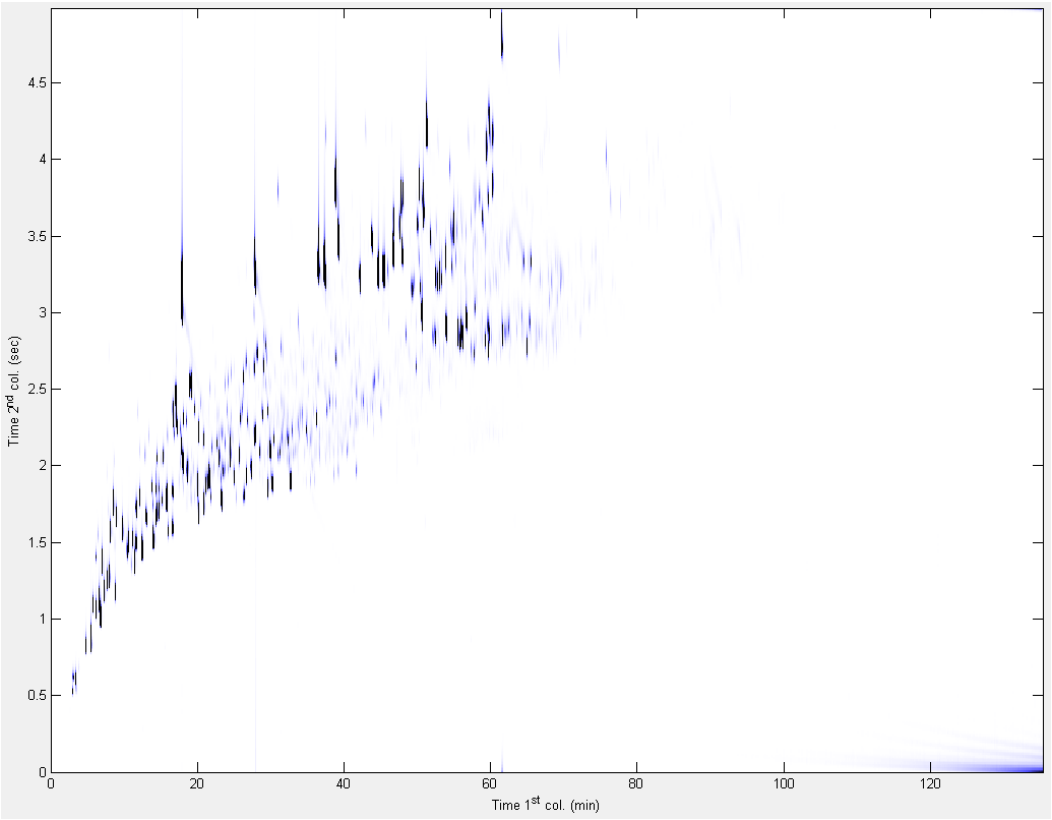


Figure II.13 *– Sample: Pygas; Modulator: Cryogenic; Configuration: Normal (A2)*

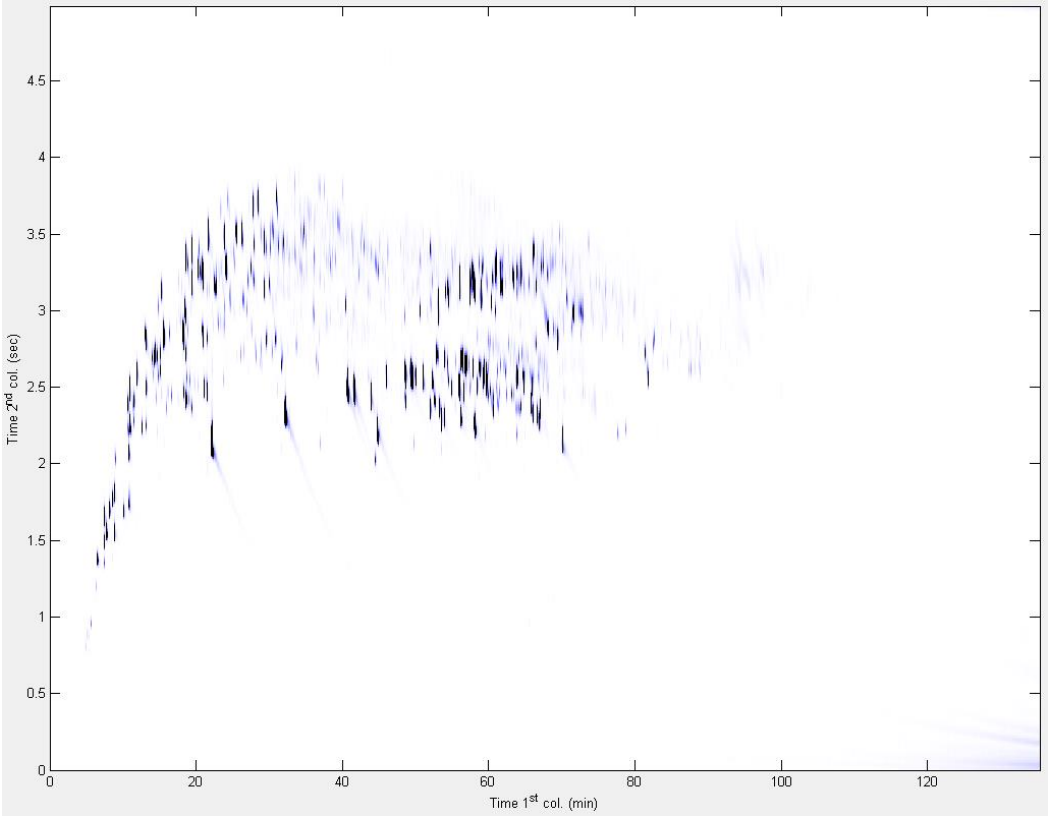


Figure II.14 *– Sample: HDT Pygas; Modulator: Cryogenic; Configuration: Reverse (B1)*

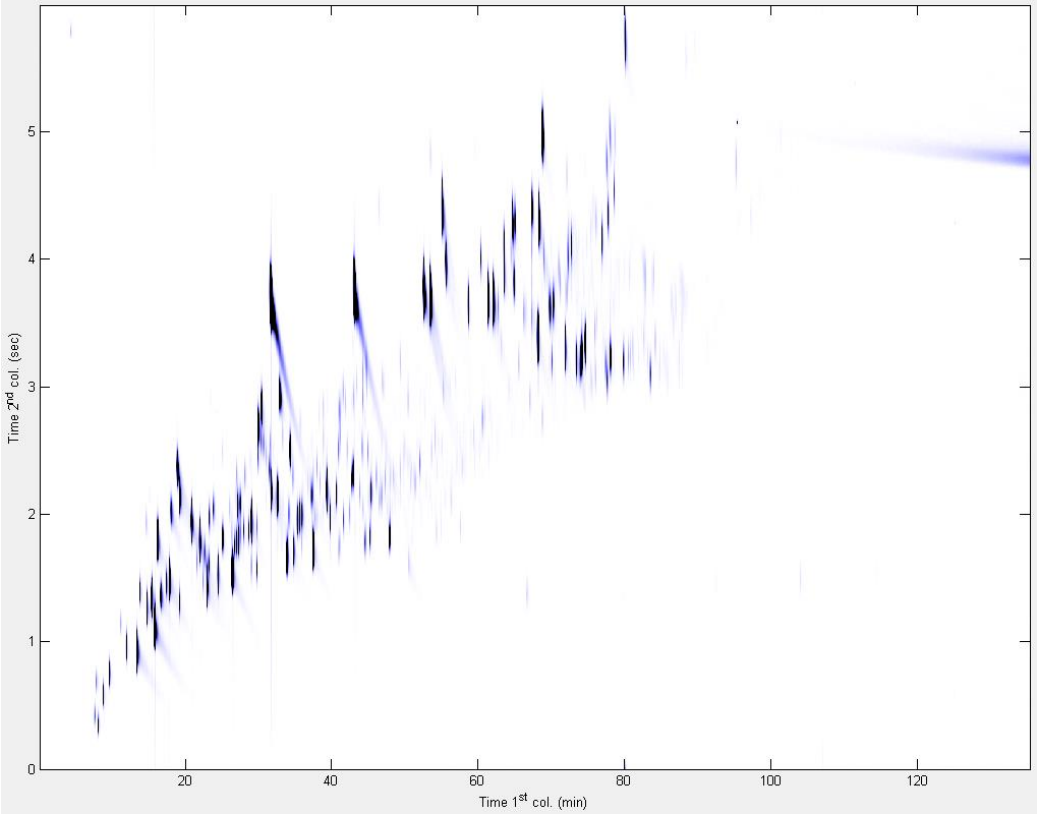


Figure II.15 *– Sample: Pygas; Modulator: Microfluidic; Configuration: Normal (C6)*

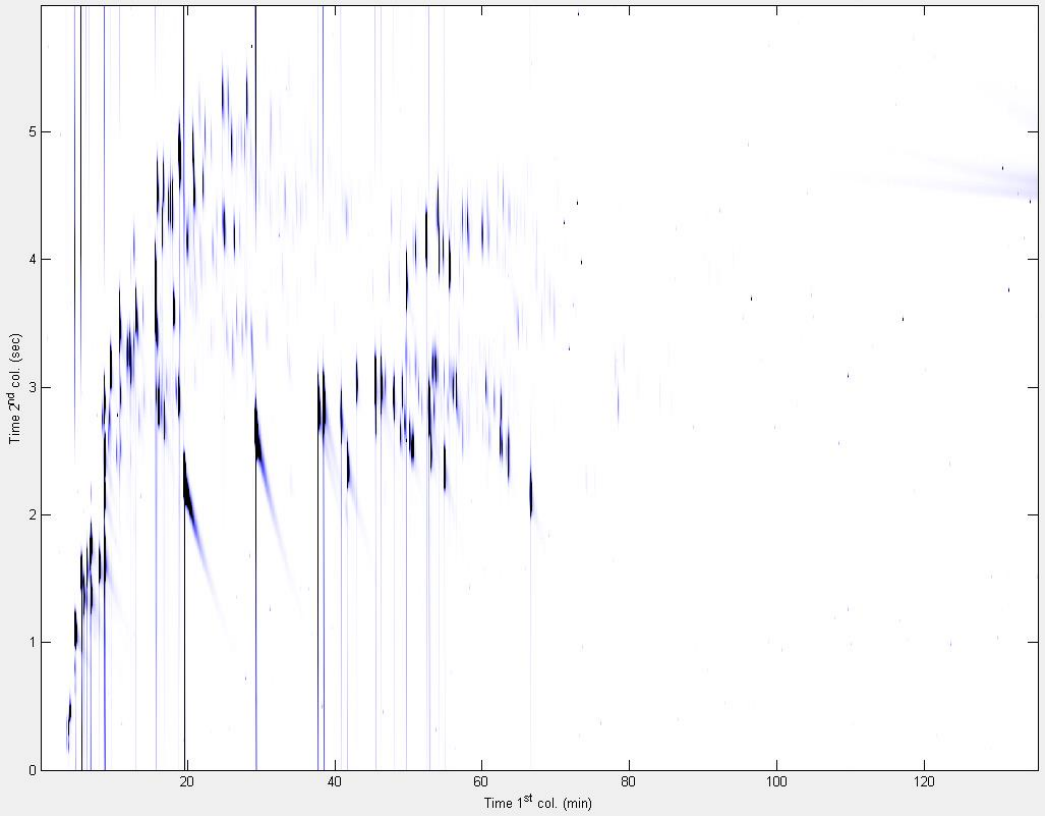


Figure II.16 *– Sample: Pygas; Modulator: Microfluidic; Configuration: Reverse (D1)*

II.5 - S8997 (1500954-001) - FCC effluent

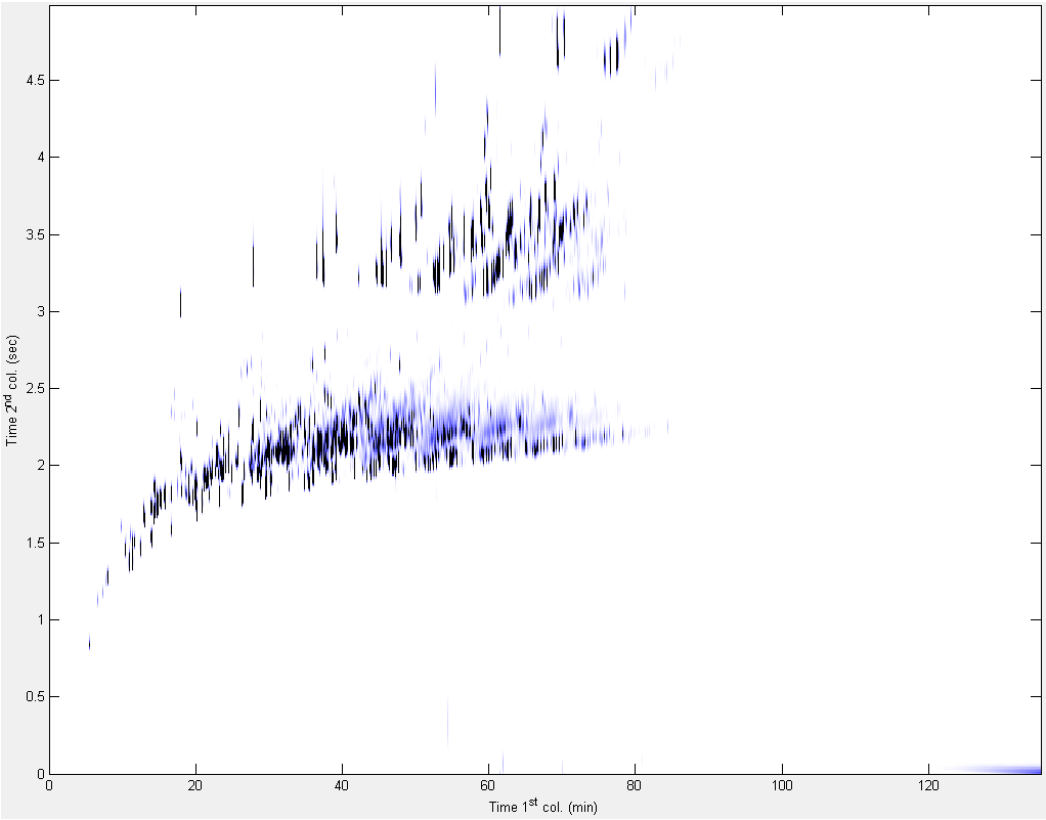


Figure II.17 *– Sample: S8997; Modulator: Cryogenic; Configuration: Normal (A2)*

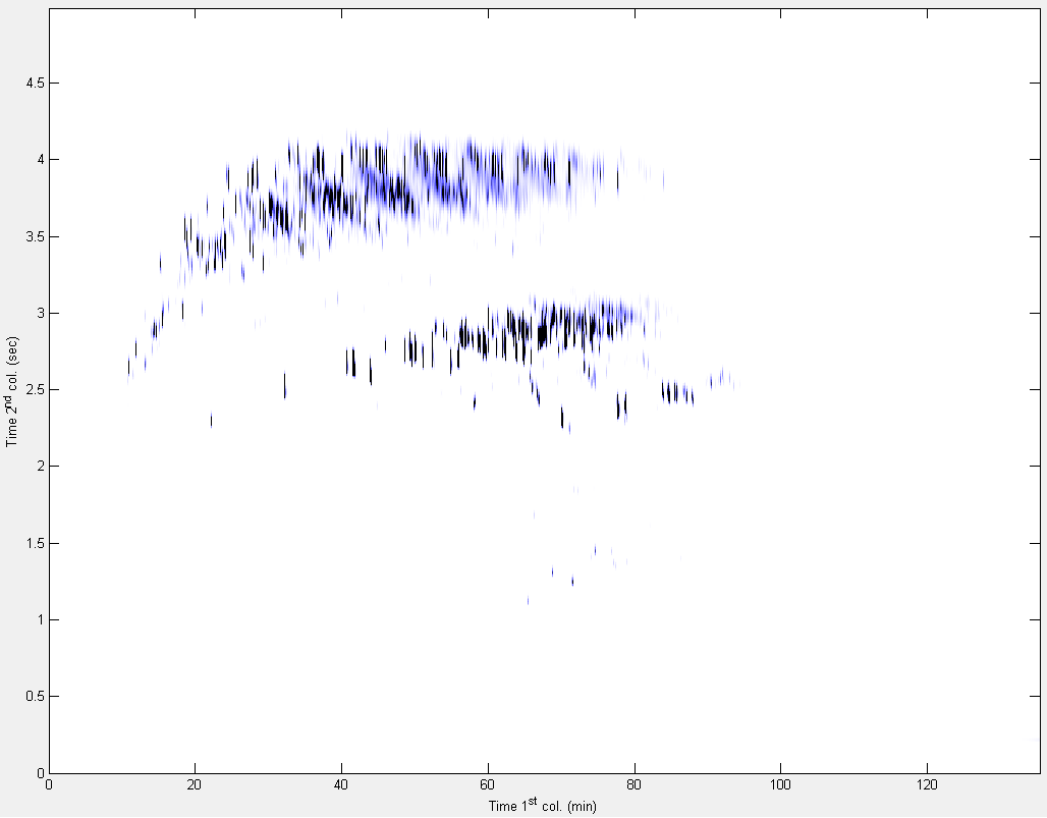


Figure II.18 *– Sample: S8997; Modulator: Cryogenic; Configuration: Reverse (B1)*

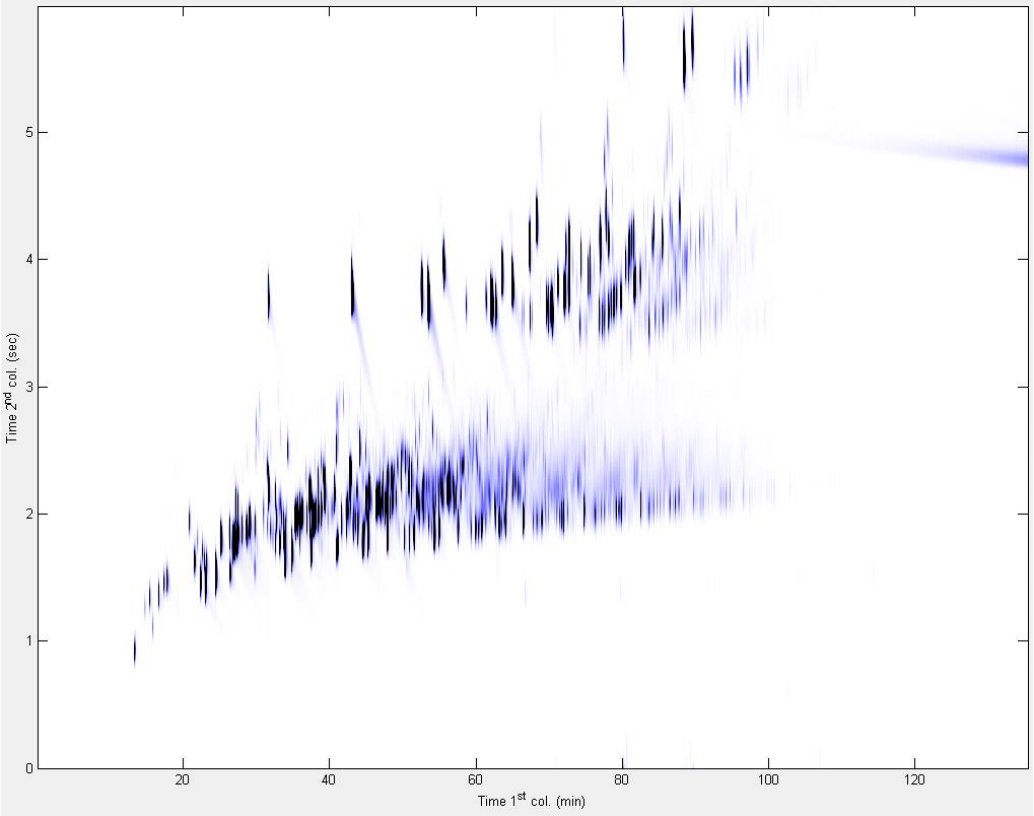


Figure II.19 *– Sample: S8997; Modulator: Microfluidic; Configuration: Normal (C6)*

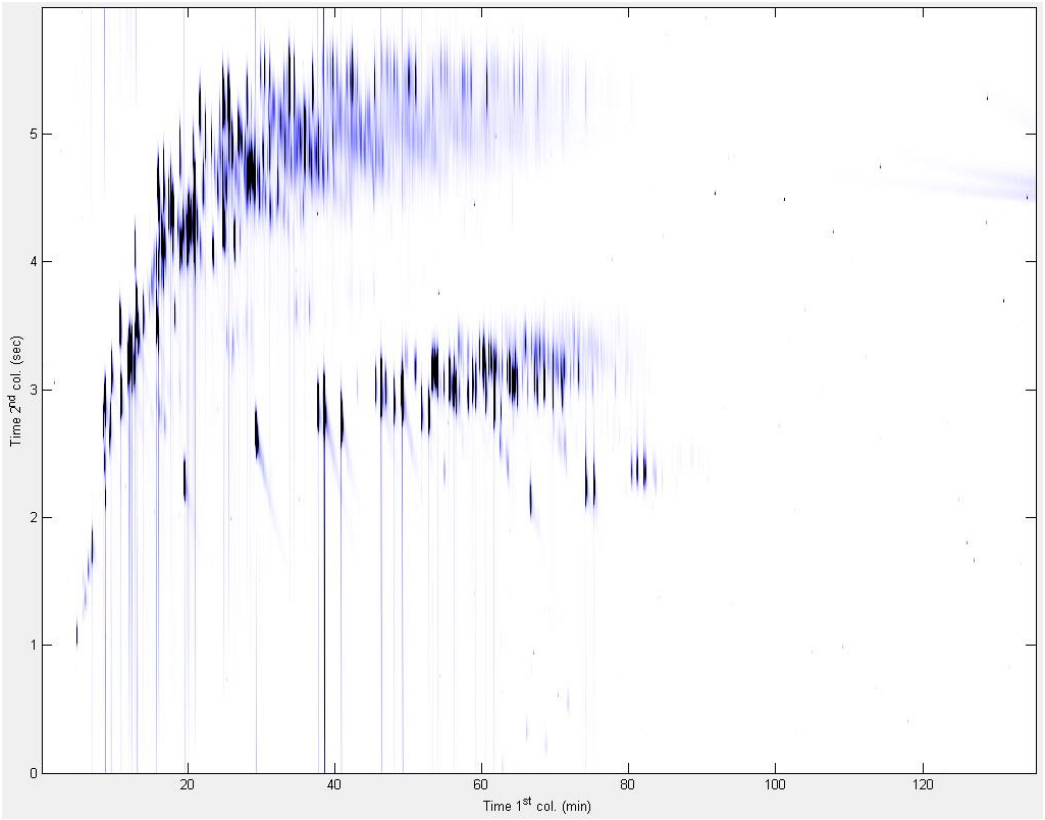


Figure II.20 *– Sample: S8997; Modulator: Microfluidic; Configuration: Reverse (D1)*

II.5 - Coupe 15-150 (1405531-001) - Oligomerization gasoline

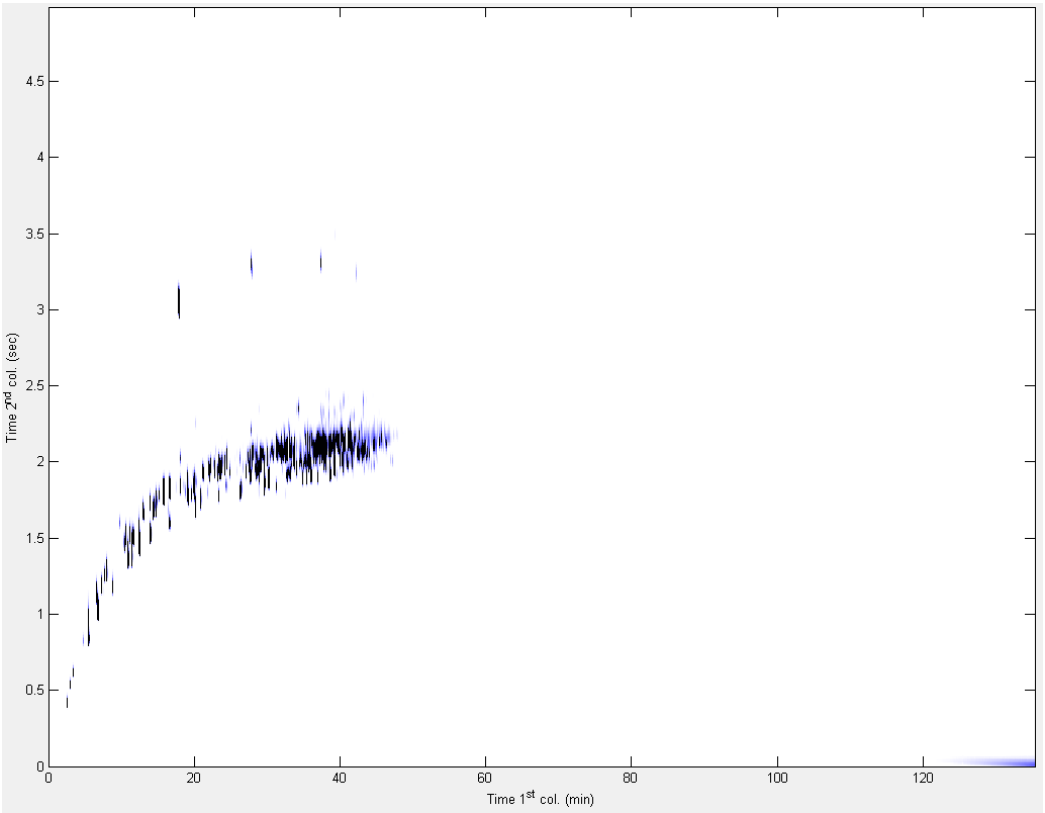


Figure II.21 *– Sample: Oligo; Modulator: Cryogenic; Configuration: Normal (A2)*

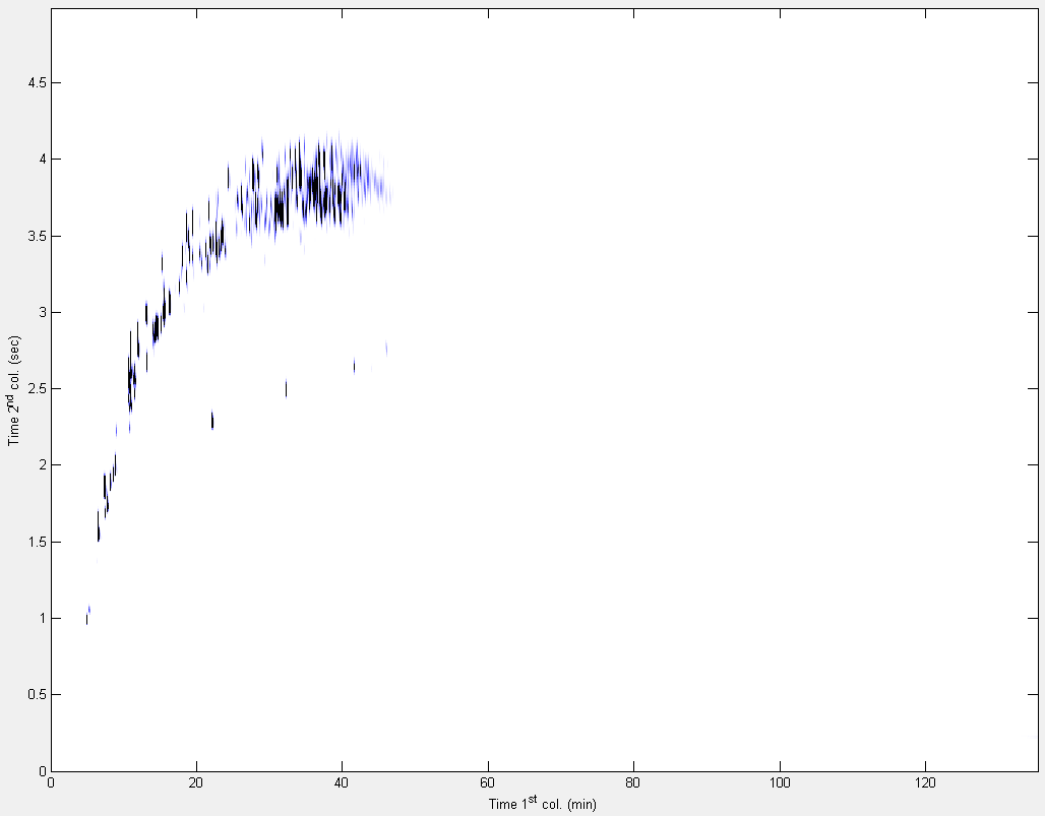


Figure II.22 *– Sample: Oligo; Modulator: Cryogenic; Configuration: Reverse (B1)*

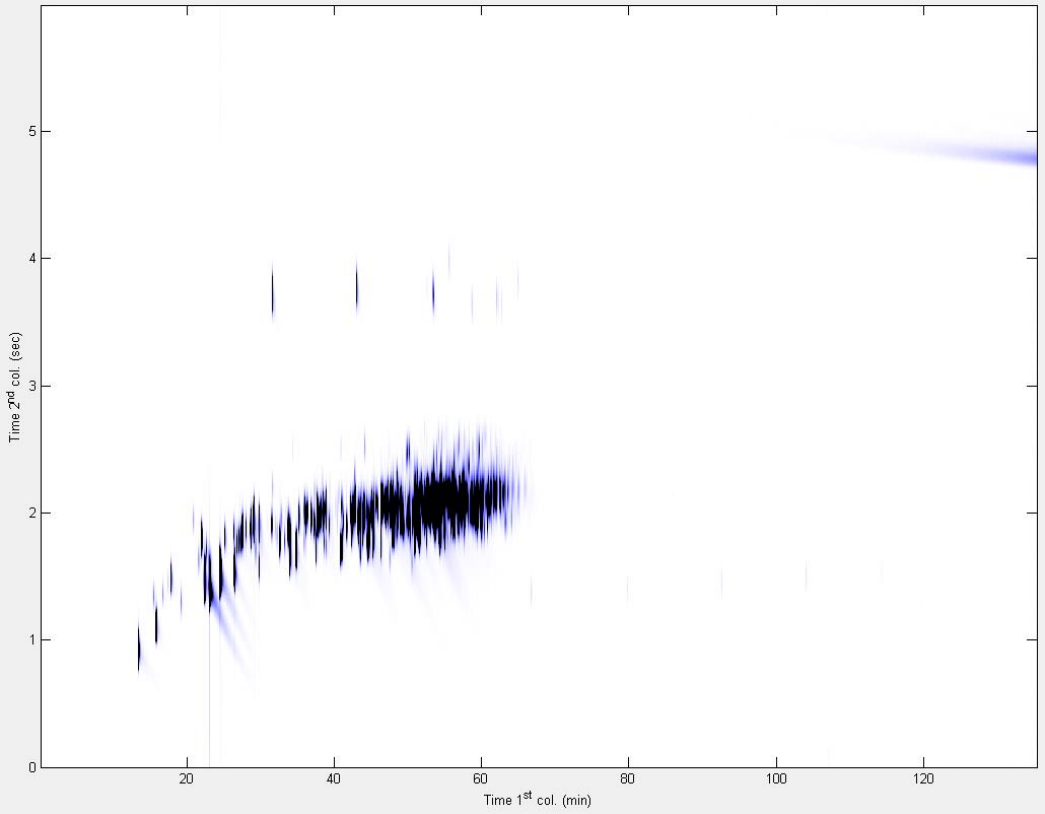


Figure II.23 *– Sample: Oligo; Modulator: Microfluidic; Configuration: Normal (C6)*

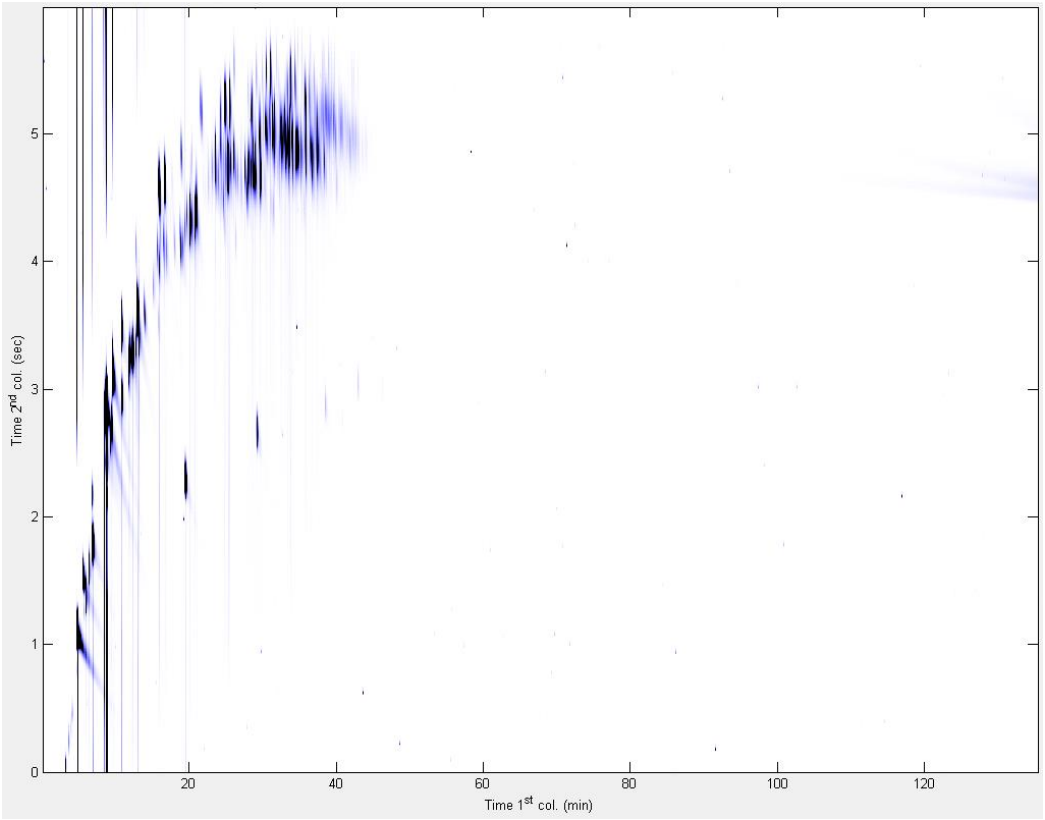


Figure II.24 *– Sample: Oligo; Modulator: Microfluidic; Configuration: Reverse (D1)*

Appendix III – List of compounds in the FCC effluent sample

Section 5.2 deals with the detailed hydrocarbon analysis of the S8244 FCC effluent sample. As stated, the MS data was treated and compounds were identified by cross-checking MS data with retention data on non-polar columns from the IFP0104 standard method analysis which uses a dimethylpolysiloxane phase with a length of 50 meters to identify the compounds present in the sample based on their retention index.

Table III.1 presents the results of the IFP0104 standard method. The compounds whose family was known but for which the exact molecule was not identified (not counting missing isomers) are not shown in this table. Two compounds that share retention times and concentration percentage values are co-eluted. Compounds marked in green were identified in the MS data from the GC×GC analysis described in Section 5.2. Many other products were detected with GC×GC-MS but not all these compounds have been identified.

Table III.1 *– IFP0104 standard method identified compound list*

Retention Time (min)	Compound	%m/m	%mol/mol	%v/v
4,45	ISOBUTANE	0,069	0,103	0,087
4,635	1-BUTENE	0,336	0,521	0,397
	ISOBUTENE			
4,725	N.BUTANE	0,249	0,372	0,302
4,819	TRANS-2-BUTENE	0,77	1,193	0,897
4,976	CIS-2-BUTENE	0,894	1,385	1,012
5,42	3-METHYL-1-BUTENE	0,573	0,71	0,643
5,73	ISOPENTANE	7,533	9,077	8,56
6,015	1-PENTENE	1,398	1,733	1,537
6,162	2-METHYL-1-BUTENE	3,188	3,952	3,451
6,276	N.PENTANE	1,265	1,525	1,424
6,392	ISOPRENE	0,109	0,139	0,113
6,453	TRANS-2-PENTENE	3,442	4,267	3,744
6,663	CIS-2-PENTENE	1,965	2,435	2,111
6,8	2-METHYL-2-BUTENE	5,846	7,246	6,215
6,871	1,TRANS-3-PENTADIENE	0,112	0,142	0,116
7,239	1,CIS-3-PENTADIENE	0,083	0,105	0,084
7,309	2,2-DIMETHYLBUTANE	0,025	0,025	0,027
7,938	CYCLOPENTENE	0,724	0,924	0,663
8,062	4-METHYL-1-PENTENE	0,256	0,264	0,271
8,129	3-METHYL-1-PENTENE	0,362	0,374	0,383
8,398	CYCLOPENTANE	0,187	0,232	0,177
8,46	2,3-DIMETHYL-1-BUTENE	1,166	1,204	1,212
8,546	4-METHYL-CIS-2-PENTENE	0,229	0,237	0,242
8,637	4-METHYL-TRANS-2-PENTENE	0,804	0,83	0,847

Retention Time (min)	Compound	%m/m	%mol/mol	%v/v
8,637	2-METHYLPENTANE	3,368	3,397	3,635
8,992	HEXADIENE	0,008	0,009	0,007
9,336	3-METHYLPENTANE	2,26	2,28	2,399
9,583	2-METHYL-1-PENTENE	1,216	1,256	1,255
9,635	1-HEXENE	0,493	0,51	0,517
10,236	2-ETHYL-1-BUTENE	0,386	0,399	0,395
10,303	N.HEXANE	0,873	0,88	0,933
10,416	CIS-3-HEXENE	0,703	0,726	0,732
10,492	TRANS-3-HEXENE	0,271	0,28	0,281
10,589	TRANS-2-HEXENE	1,431	1,478	1,488
10,736	2-METHYL-2-PENTENE	1,739	1,797	1,788
10,889	3-METHYLCYCLOPENTENE	0,453	0,479	0,419
10,951	3-METHYL-TRANS-2-PENTENE	1,147	1,184	1,16
11,09	4,4-DIMETHYL-1-PENTENE	0,259	0,23	0,268
11,198	CIS-2-HEXENE	0,814	0,841	0,835
11,624	3-METHYL-CIS-2-PENTENE	1,72	1,776	1,75
11,832	2,2-DIMETHYLPENTANE	0,006	0,005	0,007
12,108	1-METHYLCYCLOPENTANE	2,182	2,253	2,057
12,407	2,4-DIMETHYLPENTANE	0,693	0,602	0,727
13,699	2,4-DIMETHYL-1-PENTENE	0,103	0,091	0,104
13,899	BENZENE	2,634	2,932	2,116
14,084	3-METHYL-1-HEXENE	0,088	0,078	0,09
14,775	CYCLOHEXANE	0,258	0,266	0,234
14,968	2-METHYL-CIS-3-HEXENE	0,219	0,194	0,223
15,279	2-METHYL-TRANS-3-HEXENE	0,196	0,174	0,201
15,51	3-METHYL-CIS-3-HEXENE	0,439	0,388	0,434
15,662	2-METHYLHEXANE	1,781	1,545	1,851
15,81	2,3-DIMETHYLPENTANE	0,446	0,387	0,459
16,071	1,1-DIMETHYLCYCLOPENTANE	0,028	0,025	0,026
16,269	CYCLOHEXENE	0,268	0,284	0,233
16,513	3-METHYLHEXANE	1,472	1,277	1,51
16,859	5-METHYL-TRANS-2-HEXENE	0,162	0,143	0,165
17,133	1,C-3-DIMETHYLCYCLOPENTANE	0,748	0,662	0,709
17,421	1,T-3-DIMETHYLCYCLOPENTANE	0,635	0,562	0,599
17,559	3-ETHYLPENTANE	0,441	0,382	0,445
17,711	1,T-2-DIMETHYLCYCLOPENTANE	0,483	0,427	0,453
17,849	5-METHYL-1-HEXENE	0,193	0,171	0,197
17,928	1-HEPTENE	0,23	0,204	0,233
18,528	3-METHYL-TRANS-3-HEXENE	0,281	0,248	0,279
18,929	CIS-3-HEPTENE	1,053	0,932	1,058
19,132	N.HEPTANE	0,588	0,51	0,607
19,132	4,4-DIMETHYLCYCLOPENTENE	0,459	0,415	0,42
19,36	2-METHYL-2-HEXENE	1,046	0,926	1,043
19,481	1,5-DIMETHYLCYCLOPENTENE	0,379	0,343	0,344

Retention Time (min)	Compound	%m/m	%mol/mol	%v/v
19,683	TRANS-2-HEPTENE	0,464	0,41	0,466
19,864	3-ETHYL-2-PENTENE	0,219	0,194	0,215
20,222	3-ETHYL-1-PENTENE	0,98	0,868	0,995
20,64	CIS-2-HEPTENE	0,491	0,435	0,49
21,082	TRIMETHYLCYCLOPENTENE	0,089	0,07	0,079
21,297	1,C-2-DIMETHYLCYCLOPENTANE	0,428	0,379	0,392
21,384	1-METHYLCYCLOHEXANE	0,893	0,791	0,819
21,792	2,2-DIMETHYLHEXANE	0,141	0,107	0,143
22,252	TRIMETHYLCYCLOPENTENE	0,075	0,059	0,067
22,514	TRIMETHYLCYCLOPENTENE	0,06	0,048	0,054
22,842	1-ETHYLCYCLOPENTANE	0,429	0,38	0,396
23,073	2,5-DIMETHYLHEXANE	0,339	0,258	0,344
23,286	2,4-DIMETHYLHEXANE	0,588	0,448	0,594
23,981	1,T2,C4-TRIMETHYLCYCLOPENTANE	0,289	0,224	0,272
24,95	1,T2,C3-TRIMETHYLCYCLOPENTANE	0,271	0,21	0,256
25,408	1-METHYLCYCLOHEXENE	0,965	0,872	0,84
25,595	ETHYLCYCLOHEXENE	0,345	0,272	0,3
25,816	TOLUENE	4,198	3,96	3,422
26,086	4-METHYL-CIS-3-HEPTENE	0,303	0,234	0,295
26,72	1,1,2-TRIMETHYLCYCLOPENTANE	0,147	0,114	0,135
26,843	2,3-DIMETHYLHEXANE	0,316	0,241	0,314
27,272	3-METHYLCYCLOHEXENE	0,547	0,494	0,482
27,728	2-METHYLHEPTANE	0,872	0,664	0,883
27,932	4-METHYLHEPTANE	0,383	0,292	0,384
28,476	3,4-DIMETHYLHEXANE	0,347	0,264	0,341
28,787	3-METHYLHEPTANE	0,75	0,571	0,75
28,919	3-ETHYLHEXANE	0,543	0,414	0,538
29,177	1,T-4-DIMETHYLCYCLOHEXANE	0,175	0,136	0,162
29,948	1,1-DIMETHYLCYCLOHEXANE	0,016	0,012	0,015
30,501	DIMETHYLCYCLOHEXENE	0,175	0,135	0,171
30,501	1-METHYL-T-3-ETHYLCYCLOPENTANE	0,301	0,233	0,279
30,81	1-METHYL-C-3-ETHYLCYCLOPENTANE	0,214	0,166	0,198
30,976	1-METHYL-T-2-ETHYLCYCLOPENTANE	0,192	0,149	0,178
31,117	2-METHYL-2-HEPTENE	0,109	0,084	0,106
31,395	4-METHYL-CIS-2-HEPTENE	0,155	0,12	0,152
31,669	1,T-2-DIMETHYLCYCLOHEXANE	0,248	0,192	0,225
31,669	TRANS-4-OCTENE	0,122	0,094	0,119
31,87	CIS-4-OCTENE	0,189	0,146	0,185
32,286	TRANS-3-OCTENE	0,52	0,403	0,514
32,51	CIS-3-OCTENE	0,107	0,083	0,105
32,706	N.OCTANE DIMETHYL-2-HEXENE	0,828	0,63	0,831
33,261	TRANS-2-OCTENE	0,214	0,165	0,21
33,511	TRIMETHYLCYCLOPENTENE	0,446	0,352	0,397

Retention Time (min)	Compound	%m/m	%mol/mol	%v/v
33,745	3-METHYL-CIS-2-HEPTENE	0,21	0,163	0,204
34,451	CIS-2-OCTENE	0,099	0,076	0,096
35,138	DIMETHYLCYCLOHEXENE	0,021	0,016	0,018
35,369	1-METHYL-1-ETHYLCYCLOPENTANE	0,149	0,115	0,135
35,96	DIMETHYLCYCLOHEXENE	0,074	0,058	0,065
36,288	2,4-DIMETHYLHEPTANE	0,136	0,092	0,134
37,034	1-ETHYLCYCLOHEXANE	0,159	0,123	0,143
37,331	2,6-DIMETHYLHEPTANE	0,066	0,045	0,066
38,339	2,5-DIMETHYLHEPTANE	0,241	0,163	0,237
39,809	ETHYLBENZENE	0,688	0,563	0,561
41,199	META-XYLENE	1,703	1,395	1,394
41,361	PARA-XYLENE	0,723	0,592	0,593
42,338	4-ETHYLHEPTANE	0,106	0,072	0,103
42,806	4-METHYLOCTANE	0,134	0,091	0,131
42,975	2-METHYLOCTANE	0,203	0,138	0,202
43,817	3-ETHYLHEPTANE	0,069	0,046	0,067
44,027	3-METHYLOCTANE	0,2	0,136	0,196
44,691	ORTHO-XYLENE	0,782	0,64	0,628
48,507	N.NONANE	0,081	0,055	0,08
50,039	ISOPROPYLBENZENE	0,024	0,018	0,02
52,731	3,5-DIMETHYLOCTANE	0,075	0,046	0,073
53,57	2,7-DIMETHYLOCTANE	0,021	0,013	0,021
54,152	2,6-DIMETHYLOCTANE	0,041	0,025	0,04
54,738	N.PROPYLBENZENE	0,127	0,092	0,104
55,983	1-METHYL-3-ETHYLBENZENE	0,455	0,329	0,372
56,291	1-METHYL-4-ETHYLBENZENE	0,182	0,132	0,15
57,231	1,3,5-TRIMETHYLBENZENE	0,207	0,149	0,169
58,288	5-METHYLNONANE	0,036	0,022	0,034
58,686	1-METHYL-2-ETHYLBENZENE 4-METHYLNONANE	0,166	0,12	0,133
58,987	2-METHYLNONANE	0,058	0,036	0,057
60,009	3-METHYLNONANE	0,073	0,044	0,07
61,093	1,2,4-TRIMETHYLBENZENE	0,554	0,401	0,447
64,52	N.DECANE	0,029	0,018	0,028
65,299	1,2,3-TRIMETHYLBENZENE	0,12	0,086	0,095
65,686	1-METHYL-4-ISOPROPYLBENZENE	0,018	0,011	0,014
66,188	1-METHYL-3-ISOPROPYLBENZENE	0,011	0,007	0,009
66,941	INDANE	0,113	0,083	0,083
67,862	1-METHYL-2-ISOPROPYLBENZENE	0,019	0,013	0,016
69,865	1,3-DIETHYLBENZENE	0,039	0,025	0,032
70,262	1-METHYL-3-N-PROPYLBENZENE	0,077	0,05	0,063
70,827	1-METHYL-4-N-PROPYLBENZENE	0,046	0,03	0,038
71,338	1,3-DIMETHYL-5-ETHYLBENZENE	0,071	0,046	0,058
72,549	1-METHYL-2-N-PROPYLBENZENE	0,025	0,016	0,021

Retention Time (min)	Compound	%m/m	%mol/mol	%v/v
73,559	5-METHYLDECANE	0,016	0,009	0,015
74,153	1,4-DIMETHYL-2-ETHYLBENZENE	0,06	0,039	0,048
	4-METHYLDECANE			
74,386	1,3-DIMETHYL-4-ETHYLBENZENE	0,061	0,04	0,049
74,58	2-METHYLDECANE	0,014	0,008	0,014
75,075	1-METHYLINDANE	0,056	0,037	0,042
75,313	1,2-DIMETHYL-4-ETHYLBENZENE	0,068	0,044	0,055
75,519	3-METHYLDECANE	0,014	0,008	0,013
78,242	1,2-DIMETHYL-3-ETHYLBENZENE	0,033	0,021	0,026
79,864	N.UNDECANE	0,011	0,006	0,011
80,124	1,2,3,5-TETRAMETHYLBENZENE	0,036	0,023	0,028
80,619	1,2,4,5-TETRAMETHYLBENZENE	0,047	0,031	0,038
82,737	BENZOTHIOPHENE	0,011	0,007	0,008
82,961	5-METHYLINDANE	0,041	0,027	0,031
84,343	4-METHYLINDANE	0,091	0,06	0,067
85,043	1,2,3,4-TETRAMETHYLBENZENE	0,017	0,011	0,014
88,1	NAPHTALENE	0,072	0,049	0,05
88,321	4-METHYLUNDECANE	0,013	0,007	0,012
89,213	2-METHYLUNDECANE	0,023	0,012	0,022
93,302	N.DODECANE	0,006	0,003	0,005
100,614	2-METHYLDODECANE	0,007	0,003	0,007
101,404	2-METHYLNAPHTALENE	0,035	0,021	0,023
103,031	1-METHYLNAPHTALENE	0,022	0,014	0,015

The above list contains 180 compounds, 114 of which were identified using the bidimensional MS data.

Appendix IV - Silicon Speciation Experiments

The silicon speciation experiments focused on the analysis of an FCC effluent sample that had been spiked with different siloxane species at a concentration of 1 ppm. The configuration used for the analysis was configuration (A2) which was the best from the cryogenic normal tests and it was performed using the optimized conditions apart for some changes. The injected volume of sample was increased from 0.1 µl to 1 µl and the split ratio was decreased from 1:500 to 1:20. These changes were done to increase the injected volume in the column set. Another change was to set the modulation period at 10 seconds. Injecting a large volume of sample means that compounds at trace levels are more easily detected, which means the risk of wrap-around with minor species is significantly higher.

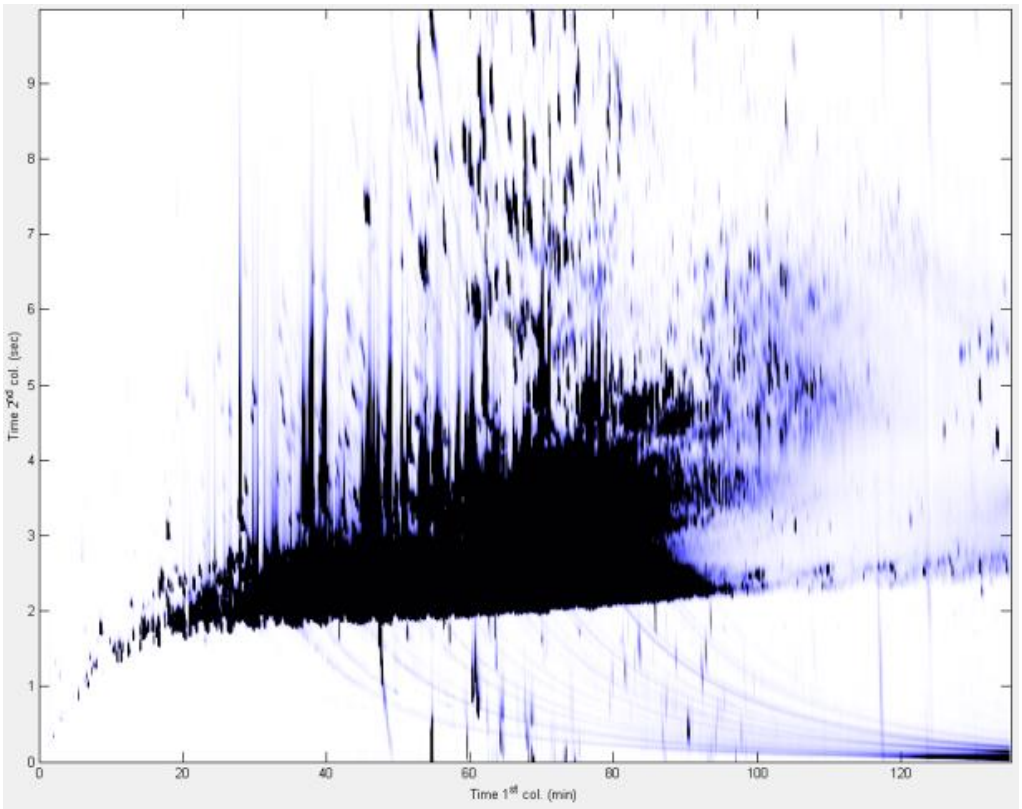


Figure IV.1 *– Chromatogram from the trace analysis of the spiked FCC sample (1 ppm)*

Looking at the chromatogram in Figure IV.1, it is not possible to exactly say where the siloxane species are eluted as they are most likely masked by the more concentrated compounds in the sample. To find out the retention times of the siloxane compounds, a model solution with a concentration of 100 ppm of each compound was injected under the same conditions. The resulting chromatogram is in Figure IV.2.

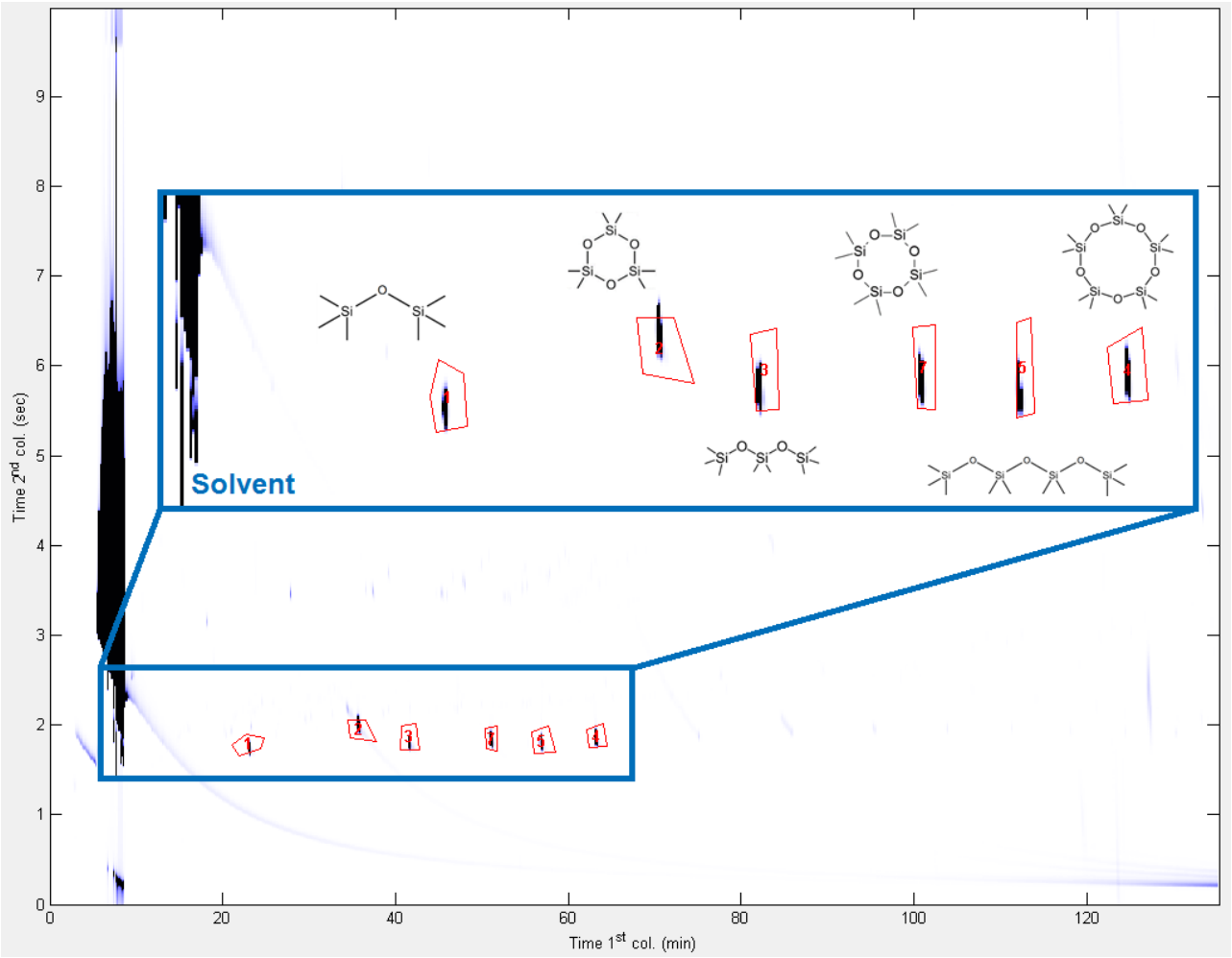


Figure IV.2 *– Chromatogram of the 100 ppm model solution with identified siloxane species; from left to right (increasing in boiling point): hexamethyldisiloxane, hexamethylcyclotrisiloxane, octamethyltrisiloxane, octamethylcyclotetrasiloxane, decamethyltetrasiloxane, decamethylcyclopentasiloxane*

The model solution also included trimethylsilanol, however this compounds was not clearly identifiable in the chromatogram. Knowing now where to look for the compounds, it is easy to go back to the 1 ppm chromatogram and locate them, as can be seen in Figure IV.3. Unfortunately, the second peak is co-eluted with the column bleeding, as well as some other compounds, nevertheless, all the other compounds can be clearly seen. A more detailed look at the one-dimensional signal of one of the peaks provides a better sense of the sensitivity associated with the GC×GC analysis method. Figure IV.4 shows the signal corresponding to the peak of one of siloxanes in one-dimensional view. The highest peak reaches a signal intensity of about 600 for a compound 1 ppm in concentration. This means that the system, using the analysis method described earlier, has a very high sensitivity, feasibly capable of detecting compounds in concentrations as low as a few hundred parts per billion.

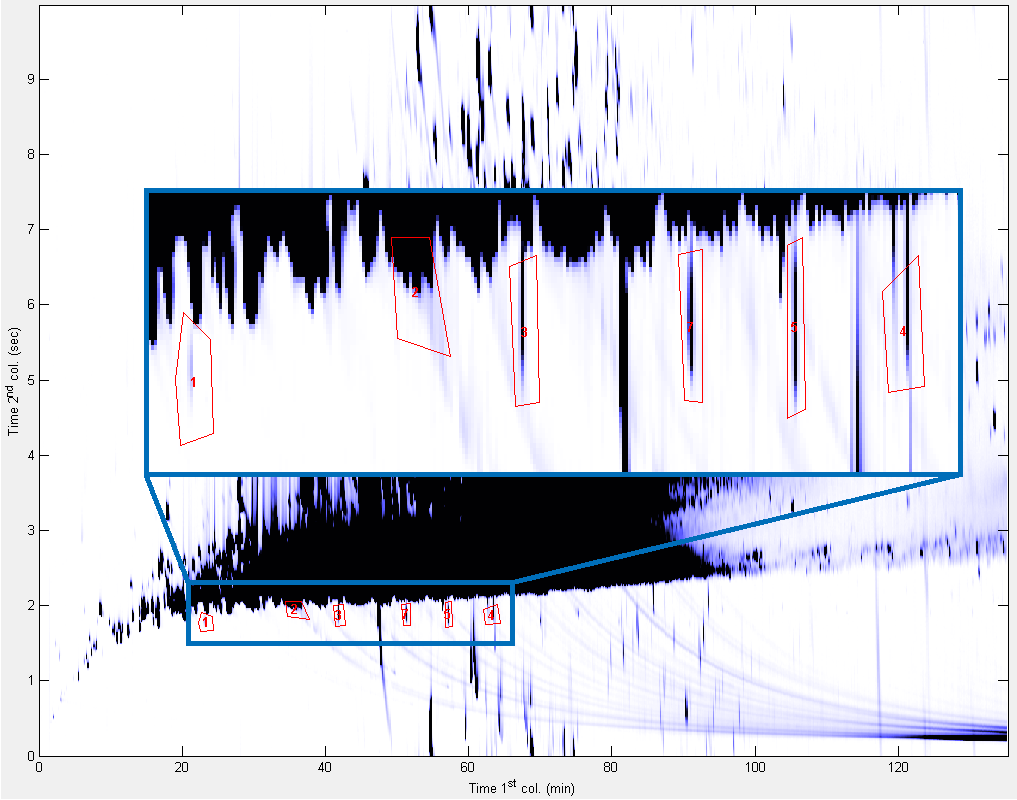


Figure IV.3 *– Verification of the presence of the siloxane peaks in the 1 ppm sample*

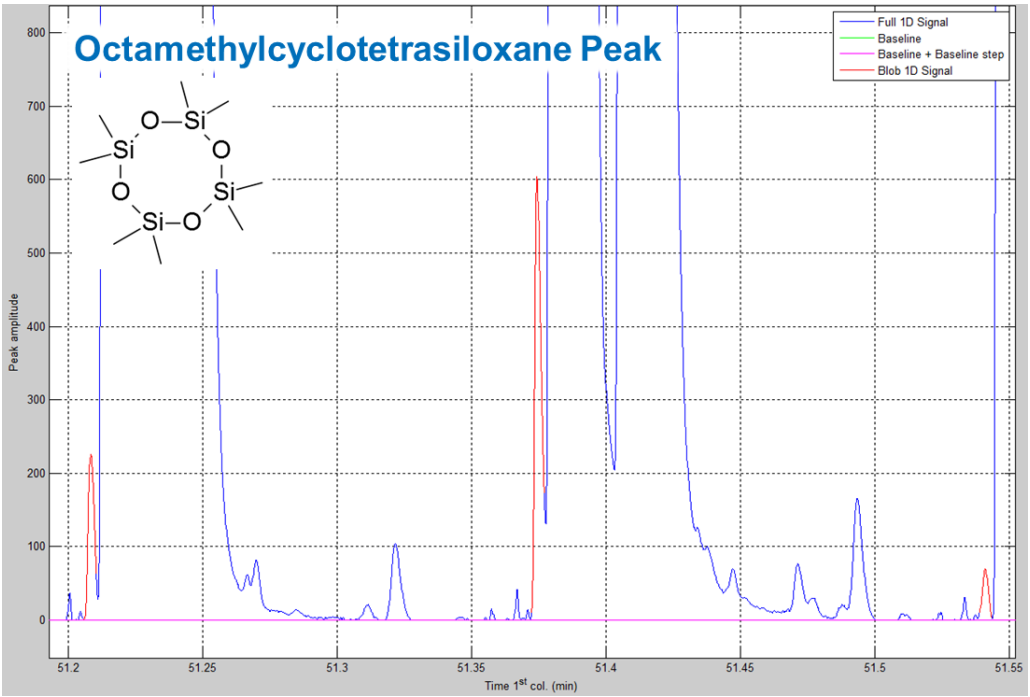


Figure IV.4 *– A siloxane peak over three modulation periods (in red)*